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MANUAL

OF

CHEMISTRY.

A GUIDE TO LECTURES AND LABORATORY WORK FOR BEGINNERS IN CHEMISTRY. A TEXT-BOOK SPECIALLY ADAPTED FOR STUDENTS OF MEDICINE, PHARMACY, AND DENTISTRY.

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AND

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Samuel P. Sadtler — Phil College of Pharm
P. C. P. Feb. 1st 1904.

A

TEXT-BOOK OF CHEMISTRY.

INTENDED FOR THE USE OF PHARMACEUTICAL AND MEDICAL STUDENTS.

BY

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BEING THE THIRD REVISED AND ENLARGED EDITION OF

SADTLER AND TRIMBLE'S CHEMISTRY.

IN TWO VOLUMES.

VOL. I.—GENERAL CHEMISTRY.

PHILADELPHIA:

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PREFACE TO THE THIRD EDITION.

In the preparation of this edition of Volume I. the authors have not only taken occasion to thoroughly revise and bring the general text up to date, but also to entirely rewrite certain chapters and to introduce new sections. Part I., on Elementary Physics, has been completely rewritten and enlarged to the extent of forty-five pages and over fifty new illustrations, special attention having been given to the subject of Electricity. Recognizing the great and growing importance of the subject of Electrolysis and Electro-metallurgy in modern manufacturing processes, the authors have introduced a special chapter, which treats the subject in as thorough a manner as possible. Chapter I., Part II., embracing the theoretical introduction to general and inorganic chemistry, has also been entirely rewritten, presenting an increase over the old text of twenty pages. The improvement aimed at was to present the fundamental principles of chemical theory in a manner which is believed to be more systematic and comprehensive. The same may be said with regard to the section devoted to the Periodic System, which has also been rewritten and enlarged. A special section has been devoted to a theoretical discussion of the Halogens as a group. At the time of going to press, the question as to the adoption of a system of atomic weights by the Pharmacopœia Revision Committee of 1900 was still unsettled, and, of the three systems, the standard of H = 1 and O = 15.88 was considered the best one to select under the circumstances.

The authors desire to acknowledge the kindness of the Macmillan Company, publishers of Thompson's "Electricity and Magnetism," and Messrs. Ginn & Co., publishers of Dolbear's "Natural Philosophy," for the use of a number of illustrations.

Samuel P. Sadtler.
Virgil Coblentz.

Philadelphia and New York,
October, 1900.

PREFACE TO THE FIRST EDITION.

An experience of some seventeen years as teachers in a professional school, where Chemistry is considered one of the foundation-stones upon which young men must build a technical education, has convinced the authors that the subject must be taught in a way that, while thoroughly scientific, is yet distinctly adapted to the ultimate uses of the students.

The professions of Pharmacy and Medicine are closely related, and their uses for Chemistry are very much alike. The members of these professions must understand the composition and chemical properties and possibilities of the whole *materia medica*, both inorganic and organic, in order safely to maintain the important trusts committed to them,—trusts involving the continued health and life of their fellow-men. The importance of thorough chemical knowledge for these related professions is now recognized in the fullest way in their official publication, the U. S. Pharmacopœia, the last edition of which has embodied throughout the most detailed and exact statements of the chemical nature, properties, and reactions of medicinal substances, together with methods of analysis or assay and tests for purity.

We have sought in the following pages to offer a text-book on Chemistry which should combine scientific accuracy and completeness with that special reference to the needs of the pharmaceutical and medical student, as well as those in active professional practice, which will make it of value for both study and reference. Compounds recognized in the U. S. Pharmacopœia are specially indicated, but they are not taken out of their proper position for such discussion.

A brief outline of Elementary Physics, much of which is absolutely essential for the understanding of chemical methods, forms Part I. The convenient division of the elements into Non-Metals

and Metals is followed in the main in Parts II. and III., subject to the limitations made necessary by the chemical relationship as indicated by the valence groups. Part IV. deals with Organic Chemistry. While the arrangement here followed is strictly scientific, it has been sought to give the subject a distinctly practical bearing, and to this end the industrial applications of organic compounds have been noted, and in a number of cases illustrated.

In Part V. a brief outline of Qualitative and Quantitative Analysis is given, the methods being such as have proved of value in our own practice. A number of the Pharmaceutical Assays of the U. S. Pharmacopœia are also added.

The Appendix contains, besides a list of the chemical elements with atomic weights and valences, thermometric scales and the specific gravity tables in most general use.

The authors have made free use of many chemical works, such as Flückiger's "Pharmaceutische Chemie," Schmidt's "Pharmaceutische Chemie," Meyer and Jacobson's "Organische Chemie," Bernthsen's "Organische Chemie," Weyl's "Organische Chemie für Mediciner," Fischer's "Neuere Arzneimittel," Gamgee's "Physiological Chemistry," Pictet's "Alcaloides Végétaux," Power's "Essential Oils," Allen's "Commercial Organic Analysis," Prescott's "Organic Analysis," and Sadtler's "Industrial Organic Chemistry."

Our thanks are due to J. C. Peacock for valuable assistance in the preparation of Parts III. and V., to S. S. Sadtler and H. Blount Hunter for work on the index, and to Edwin Thorpe for the execution of many original drawings for the illustration of the work.

S. P. S.
H. T.

PHILADELPHIA, February, 1895.

PREFACE TO THE SECOND EDITION.

In answering the demand for a new edition of this work, the authors desire to express their appreciation of the kind reception which was awarded to the book on its first issue and the continued favor which it has met.

They believed that a scientifically accurate and fairly complete work on chemistry, written from the stand-point of the pharmacist and giving especial attention to all compounds mentioned in the United States Pharmacopœia, would be of value not only to the student but to the practising pharmacist and physician, and are glad to know that this belief was justified.

The work, however, grew on their hands, and in consequence the first edition formed a large octavo of some 950 pages, the shape and bulk of the book making it inconvenient for many purposes.

To obviate this difficulty without sacrificing any of the features of the work that have proved valuable, the authors have now determined to issue the new edition in two volumes, one containing the Elementary Physics, Inorganic and Organic Chemistry, which together form the basis of the regular course of chemical instruction in our pharmaceutical and medical schools, and the other containing the Qualitative and Quantitative Analyses and Pharmaceutical Assaying found in the previous edition, together with a new section on Urinary Analysis and a few selected topics of importance to the practising pharmacist or physician, such as Water and Milk Analyses. They believe that in this way they will not only make the book more convenient to handle, but will give it a wider field of usefulness and greater value to students and practitioners alike.

Volume I. has been carefully revised and much new matter incorporated, especially in Part IV. under Organic Chemistry.

Several additional illustrations have been inserted, such as those in illustration of the views now held on stereo-chemistry and the new methods for the determination of molecular weights of organic compounds.

Some few sections on the technical applications of organic chemistry which were found in the first edition have been omitted, as it was thought that they might be spared from a book intended to bear specially upon pharmaceutical chemistry.

Volume II. has been almost entirely rewritten and much enlarged from what constituted Part V. of the original book. The part on Quantitative Analysis has been expanded and made serviceable as the basis of a fuller laboratory course on this subject ; Pharmaceutical Assaying has been made to cover all the valuable assays of the United States Pharmacopœia ; and, as already stated, the sections on Urinary Analysis and Milk and Water Analyses have been added.

The authors wish to express their especial indebtedness to Mr. Josiah C. Peacock for much valuable assistance in the preparation of Volume II., as, owing to the protracted illness of one of us, this part of the work was finished by him.

They desire also to acknowledge the assistance of Miss Florence Yaple, who undertook the compilation of the index for the book.

SAMUEL P. SADTLER,
HENRY TRIMBLE.

POSTSCRIPT.—The death of Professor Henry Trimble, which took place August 24, 1898, while Volume II. was passing through the press, made it desirable that some provision for the future work on this book should be made. The surviving author is glad to be able to state, therefore, that he has associated with himself Dr. Virgil Coblentz, Professor of Chemistry and Physics in the New York College of Pharmacy, who from this time on will share the editorship of the book with him. While no radical change in the plan of the work is contemplated, the authors purpose to keep it in all respects abreast of the latest developments of chemical science.

SAMUEL P. SADTLER.
VIRGIL COBLENTZ.

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PART I.

ELEMENTARY PHYSICS.

CHAPTER I.

MATTER, FORCE, AND MOTION.

1. Introductory.

Science is the attempt to classify facts or observations according to apparent points of resemblance or difference and to suggest underlying causes for these.

Matter is that which occupies space and is apprehended by the aid of our senses.

Physical Sciences.—All branches of physical science, as opposed to metaphysical science, are concerned with the study of matter, its properties, forms, motions, and the laws which determine and regulate these. We may again distinguish between the descriptive or natural history sciences, such as *mineralogy* and *geology*, *botany* and *zoölogy*, which are chiefly concerned with the outward forms and appearance of matter, and the exact physical sciences, such as *chemistry* and *physics*, which are concerned with the internal composition of matter and the motions of which it is capable.

Relationship of Physics and Chemistry.—It is obvious that, while the range of phenomena covered by physics and chemistry is a very wide one, the relation of the two branches is very close, that they are mutually dependent one upon the other, and that a clear understanding of the results of the one science involves at least a knowledge of the generalizations of the other and a summary of its results. An outline of those branches of physics which bear most closely upon chemical phenomena should, therefore, precede the detailed study of the latter science.

2. General Definitions.

Extension.—Matter has already been spoken of as occupying space. It therefore has extension, and this conception of it

necessarily results from the fact that its existence is made evident by our senses, whether immediately, as by the aid of sight or touch, or more indirectly by the aid of the senses of hearing, smelling, or tasting.

Divisibility.—If matter have extension, we must also admit its divisibility. That most forms of matter about us can be divided into smaller fragments or portions is a matter of every-day experience. We break a stone or piece of rock into fine fragments. These can then be ground to still finer powder, and so the subdivision carried on. There is, of course, a practical limit to this, because of the deficiencies of the tools with which we work. Under a powerful microscope the finest solid particles obtained by grinding, or the minutest film of liquid, show plainly the possibility of further subdivision.

Molecules and Atoms.—The smallest particles of matter which we can conceive of as obtained by this mechanical or physical subdivision we call *molecules*. How large these molecules are, what their shape is, or what their absolute weight is, we do not know. We merely know that they still show the distinctive properties which pertained to the masses of matter with which we started, and that therefore physical or mechanical means have not been able to tell us anything of the composition of the material in question. But many of these forms of matter, although not capable of resolution into anything different by methods of mechanical subdivision, are capable of decomposition into simpler forms under the influence of chemical reagents. We assume, then, that molecules are made up of still smaller particles, to which the name *atoms* has been given. These smallest particles of matter are supposed to be unalterable.

Simple and Compound Matter.—The union of like atoms gives us simple or elementary matter, of which chemists have distinguished some seventy kinds (see p. 151), while the union of unlike atoms gives us compound matter, the varieties of which are almost endless.

Indestructibility of Matter.—If, as stated, the atoms or smallest conceivable portions of matter are final, unalterable particles, it follows that matter is indestructible, whatever be the influences to which it may be subjected and the changes of form which it may undergo. Compound matter may, indeed, be resolved into simpler combinations, and ultimately into elemental matter, under the influence of chemical treatment, but the sum total of the products so obtained must always equal that of the matter

operated upon. Cases of apparent loss or destruction of matter are all explained upon careful examination of the reaction in its several phases. Changes of outward form take place under the influence of physical agencies alone, so that a solid or liquid may lose in weight by the escape of a gas or vapor, and changes in the method of combinations of the atoms may take place under the influence of chemical reagents, but if the products are examined it will be found that no new atom has been created nor has any been destroyed. This is sometimes called Lavoisier's Law of the Indestructibility of Matter (see p. 161).

Three States of Matter.—We recognize three states of aggregation in matter,—the *solid*, the *liquid*, and the *gaseous*. In the first of these the molecules are held firmly together by the force of attraction, which is greater than the repellent force which tends to separate them, so that the mass of matter tends to retain its shape, and the exertion of some force is necessary to overcome the adhesion of the molecules and change the shape; in the second the attractive and repellent forces are balanced, the molecules move easily past one another, and the liquid readily assumes the shape of the containing vessel; in the third the repellent is more powerful than the attractive force, the molecules constantly tend to separate and occupy a greater space, and pressure is required to overcome this tendency.

3. General Properties of Matter.

Extension and divisibility have already been referred to as self-evident from our conception of the existence of matter as demonstrated to us by the aid of our senses. We are led by the use of these senses to ascribe length, breadth, and thickness to material objects, and thus arrive at the necessity for units of measurement (see p. 18). It matters not that an object may be extremely minute, so that it is perceptible only by the aid of powerful magnifying apparatus; so long as we grant its existence, even as a single molecule (see p. 14), we must conceive of it as possessing definite shape or form, and hence extension.

Impenetrability is also an essential property of matter. As matter occupies space, any particular space cannot be occupied by two different bodies at the same time. Thus, if a solid body, like a bar of metal, be immersed in a tumbler previously filled with water, it will cause some water to overflow. The amount so displaced will exactly equal the volume of the solid immersed. Numerous apparent exceptions to this rule exist, as

when a nail is driven into a piece of wood, or water is poured into a tumbler previously filled with dry sand, or a piece of dry wood is dipped into water. But in all such cases we must take account of another property of matter, viz., *porosity*. In the use of this term we mean that the molecules of a substance are never in actual contact, but are separated by spaces relatively large as compared with the size of the molecules themselves. These spaces are called *pores*, and their existence is made evident when pressure is applied and the mass is diminished in bulk. This diminution in the space occupied under increase of pressure shows most notably with gases, which are therefore termed the most compressible, but occurs also in liquids and solids. This is explainable only by the assumption of the porosity of matter.

All bodies are more or less porous. Those pores which form actual cavities or cells, and are visible, are called *sensible pores*, as seen in the structure of such bodies as wood, sponges, unglazed brick, filter-paper, etc. The invisible spaces that separate the molecules of substances are called *physical pores*. A clear illustration of this is had when we mix equal volumes of alcohol and water. Instead of the mixture equalling the sum of the two liquids, it is only about ninety-five per cent. of the combined volume.

Metals contain physical pores, and although these cannot be seen by aid of the most powerful microscope, still they are shown to be pores by the fact that, by means of great pressure, liquids and gases can be made to pass through them.

As a proof of and dependent upon the porosity of bodies is the property of *compressibility*. Gases are the most compressible of bodies. In them the molecules are more widely separated than in liquids or solids, and are tending to separate still more widely ; but for this very reason they respond more readily to the influence of pressure and can be compressed into smaller space. As we will see later, temperature as well as pressure has much to do with this change of volume.

The compressibility of liquids is but slight ; solids, on the other hand, may be very compressible, the change in this case depending, however, largely upon the existence of sensible pores, as in the case of wood, cloth, paper, etc., which readily yield to pressure. Metals are also compressible, as is shown in the process of stamping coins with hardened dies.

Elasticity is the property by virtue of which bodies that have undergone compression tend to resume their original form or

volume upon the removal of the compressing force. It generally goes hand in hand with the property of compressibility ; hence gases, which are the most compressible of the forms of matter, are also the most elastic. Liquids in the degree that they are compressible under pressure are also perfectly elastic. Solids show the property of elasticity in varying degrees. India-rubber, ivory, glass, and tempered steel are highly elastic, while clay and putty have this property only to a very slight degree. The elasticity of cork adapts it for use as stoppers ; the elasticity of air renders it a vehicle for the transmission of sound : also this property has been utilized in making air-beds, air-cushions, and in propelling machinery.

Mobility and inertia, which are general properties of matter dependent upon motion, will be referred to later (see p. 19).

4. Volume and Mass.

Volume.—As before stated, our most elementary conception of matter is that it occupies space. The amount of space it occupies is termed its volume. We can conceive of its extension in one direction only, which we call space of one dimension, or length ; of extension in two directions, which we call space of two dimensions, or area ; of extension in three directions, which we call space of three dimensions, or volume.

Mass is the amount or quantity of matter contained in a body. A pound of cotton may occupy a cubic foot or be compressed to a cubic inch ; in either case the number of molecules is the same and the weight the same ; hence mass is independent of volume. Mass is determined by weight ; two bodies have equal masses when placed on a balance *in vacuo* and they exactly counterpoise each other. While the weight of bodies varies according to the action of gravity upon them (see p. 21), their mass is, on the contrary, invariable.

Density is the degree of closeness of the particles of a body. If two cubic inches of air be compressed so as to occupy the space of one cubic inch, then its density will be twice as great. Different bodies having the same volume contain different quantities of matter ; for example, a cubic inch of platinum contains 21.5 times as much matter as a cubic inch of water, the same volume of lead 11 times, that of iron 7.5 times, and aluminum 2.6 times. Since we are unable to count the number of molecules in a mass, we employ weight as a means of determining this density. The masses of bodies are proportional to their

weights. We ascertain the density of solids by comparing the weight of a given volume to the same volume of water taken as standard unit. In the case of gases we compare equal volume-weights of the respective gas and either air or hydrogen as standard. For further explanation, see p. 38.

Unit of Time.—The second is $\frac{1}{86400}$ part of a mean (average) solar day, the day is the time required for the earth to turn on its axis once, the hour is one twenty-fourth part of this day, and the minute the sixtieth part of an hour. The second is the time required for a pendulum 39.1398 inches long to make one vibration; sixty of such constitute a minute, and 86,400 an average solar day.

Unit of Length.—The English unit, still in common use, is the foot, with its subdivision, the inch, and its multiple, the yard; the French unit, used universally in scientific calculations, is the meter, with its decimal subdivisions, the decimeter, centimeter, and millimeter.

Unit of Area.—The English units are the square inch, the square foot, and the square yard; the French units, the square meter, the square decimeter, and the square centimeter.

Unit of Volume.—The English units, the cubic inch and the cubic foot, are not in general use. Various units are used, as the pint, quart, and gallon for liquids, and the peck and bushel for solids. The French units are the cubic decimeter, or the liter, and the cubic centimeter.

Unit of Mass.—The English unit is the pound avoirdupois, which bears no simple relation to the units of volume; in the French system the unit is the mass of a cubic centimeter of distilled water at the temperature of its maximum density (4° C.). This is the gramme, and its multiples and submultiples are all decimal.

Tables of the metric system and of English weights and measures will be found in the Appendix.

5. Motion and Force.

In our statement of the general properties of matter, extension and impenetrability were defined. Both of these conceptions imply a fixed position as assignable at any time to the mass or molecule of matter under consideration. If this position remain constant through a period of time, we speak of the body as at rest; if it is changing, the body is said to be in motion. We must remember that these statements are not to be taken as abso-

lute. The body is at rest with reference to its original position, or in motion with reference to the same, while both the body and the original fixed point may be in motion with reference to some other distant point. Motion and rest are therefore purely relative terms.

Inertia is the tendency which matter has to maintain its state of rest or uniform motion. If in a state of rest, it remains so until disturbed by some force to produce movement. If in motion, it will move uniformly in a straight line until some force causes this movement to cease. A rifle bullet would continue its course indefinitely in a straight line were it not for the resistance of the air and the attraction of gravity. It is because the earth is moving in frictionless space that it continues to rotate so regularly upon its axis ; because of this the length of the day has not varied a second in centuries. *Mobility* is the property by virtue of which matter yields readily to the exertion of some force, causing it to change its relative position, or inducing motion.

The *velocity* of a particle of matter is the rate of its motion at any given time.

Force is that which by acting upon matter either produces or arrests motion. It is a manifestation of energy, and may be originated in a variety of ways. Thus, we speak of chemical forces, which are manifestations of atomic energy ; of molecular forces, which result from molecular energy ; and cosmic forces, which illustrate the energy of large masses.

Work is energy applied in overcoming resistance, as when a man lifts some article from the ground, where the attraction of gravitation is to be overcome, or when an engine pulls a load, overcoming the resistance due to inertia and friction.

The unit of work is the work done in raising a unit of weight through a unit of height. As we have already seen, the units of weight and measure differ in the English and the French systems, hence different units must be taken according as one or the other system is used. The *foot-pound*, or the work done in raising one pound avoirdupois one foot, is the English unit, and the *kilogram-meter*, or work done in raising one kilogram one meter, is the French unit. If a person weighing 100 pounds mounts a ladder of 20 feet he has done 2000 foot-pounds of work. For estimating power a larger unit is taken,—namely, the *horse-power*. This is equivalent to the strength of an average horse, sufficient to raise 33,000 pounds vertically one foot in

one minute. The capacity of steam engines is generally rated in this manner: thus, an engine is said to be 10 horse-power if it is capable of performing work equivalent to raising 33,000 pounds 10 feet in one minute, or 330,000 pounds one foot in a minute. H.-P. = weight in pounds $\times$ distance (or height) in feet per minute $\div$ by 33,000. For example, if two horses pull a car weighing 200 pounds at the rate of 300 feet a minute they will exert 1.81 + horse-power.

Energy is capacity for doing work. It is possessed by matter because of its mass and velocity, and its exercise involves motion of some kind. Thus, we have the energy of the visible motion of the mass and the energy of the invisible motion of the molecules, which is known to us under the forms of heat, sound, radiant energy or light, and electricity.

Energy may be potential or kinetic (actual). A weight held up by the hand, or by a support, has the power, because of its position, to fall, and thus do work, if the support be withdrawn. This is potential energy, or energy of position. Numerous applications of this suggest themselves, as the case of a wound-up spring, or an elevated tank or reservoir of water. The same weight descending in consequence of the withdrawal of the support, the spring uncoiling, and the water acting upon a turbine wheel, all represent kinetic energy, or the energy of motion.

Exact measurements have shown us in the cases of the weight, spring, etc., that the kinetic energy developed exactly equals the potential energy that may have been stored up, and no loss or gain is found when all the elements have been carefully calculated. This principle may, however, be extended not only to all cases of visible energy of motion, but to energy wherever and however manifested. As matter is indestructible, and can be neither created nor destroyed by the changes to which it is subjected, so energy is indestructible, and cannot be created or destroyed. Energy of one form may be changed into energy of another form, but there is no absolute gain or loss in amount. This law is known as the *conservation of energy*.

This change of one form of energy into another without loss of actual amount is one of the most important facts in nature, and one most familiar to us. If we rub the fingers briskly over a surface of cloth or wood, we feel a sensation of warmth. The visible motion of the hand, due to muscular energy, is transformed into that form of molecular energy known as heat. In

the steam engine we convert the potential energy of the coal, by combustion, into actual heat energy, and in turn impart visible energy of motion to the piston and connected parts of machinery. This motion, by the aid of a dynamo machine, may be converted into electrical energy, and this in turn into either heat or light energy. This illustrates what is termed the *conservation and correlation of forces*, or, more exactly, *of energy*.

6. Forms of Attraction.

Gravitation is the force by virtue of which the particles of all matter are attracted towards one another. The strength of the attraction between particles varies with the mass of each particle, and is inversely as the square of their distance apart. That is, if one body contains twice as much mass as the other, its power of attraction is twice as great as the other. In the second case, when the distance between the two masses is doubled, their attraction is reduced one-fourth ; if the distance be trebled, their mutual pull upon each other will be only one-ninth. The earth exerts this force of attraction upon all bodies near it, drawing them towards its centre. When this force is unresisted, motion results and the body falls ; when resisted, pressure which we call *weight* is produced. This attraction is general throughout the universe, and serves to retain the planets in their orbits. The earth pulls upon every particle of the bodies upon its surface, and by reason of its superior mass tends to draw them towards its centre. This force is exerted along a straight line, which, therefore, marks the shortest path towards the earth's centre, and is called a *plumb-line*. The weight of a body is proportional to its mass, because the attraction of the earth acts upon each particle which goes to make the mass. Such attraction varies with the distance from the surface of the earth ; at the centre weight ceases, because the mass is equally attracted on all sides. Where a body weighs one kilogramme on the earth's surface (4000 miles from its centre), at a height of 4000 miles it would weigh 250 grammes, or one-fourth as much, in accordance with the law that the attraction varies inversely as the square of the distance.

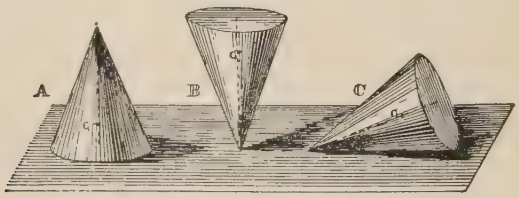
Weight is the measure of the attraction exerted by the earth upon a given mass.

The *unit of weight* is the same as the unit of mass,—one pound avoirdupois in the English system, and one gramme in the French or metric system.

The *centre of gravity* of a body is the centre of weight or attraction. It is that point in a body at which, if supported, the whole mass will remain at rest in any position in which it may be placed. In a sphere of uniform density this centre of gravity will exactly accord with the centre of the mass; in a cube it will be at the intersection of the diagonals; in a rod or bar, such as is used for the beam of a balance, it is at the centre of its axis. In irregular-shaped bodies this centre of gravity may be found by attaching a string at one point and allowing the body to hang suspended by this string; the line formed by the string is then projected through the object. This operation is repeated, supporting the mass from another point, and the point of intersection of these lines is the centre of gravity.

Equilibrium.—When a body is supported and yet free to swing before coming to rest, it will be in equilibrium when the centre of gravity is in the same vertical line as the point of support. But to insure stability the centre of gravity must also be under the point of support and not above it. According to the relative position of these two points we have the three conditions of equilibrium,—*stable*, *unstable*, and *neutral*. A suspended body is in stable equilibrium, therefore, when the centre of gravity is below the point of support, in neutral equilibrium when they coincide, and in unstable equilibrium when the centre of gravity is above the point of support.

FIG. 1.



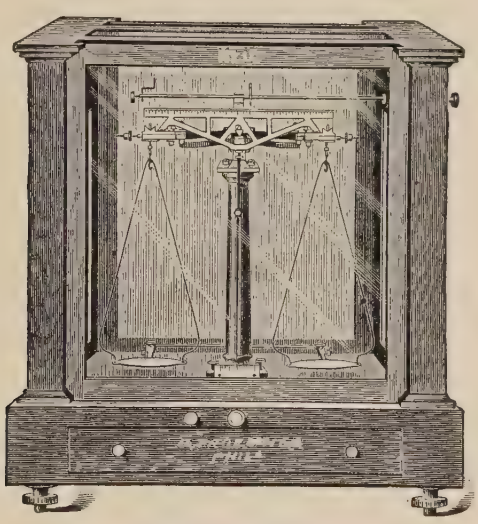
Stable, unstable, and neutral equilibrium.

Fig. 1 shows us three cones which also illustrate the three conditions respectively. A is in stable equilibrium, the centre of gravity being in a straight line below the centre of figure; B is in unstable equilibrium, as the centre of gravity is above both the centres of figure and support; C is in neutral equilibrium, as a new line between the centre of gravity and point of support is established whenever it is moved.

The chemical balance is an important application of the fore-

going principles. As shown in the illustration, Fig. 2, it consists of a beam supported in the centre so as to oscillate with the slightest amount of friction. To the ends of the beam are attached supports for the pans, on which the weights and articles to be weighed are placed. By means of a screw adjustment

FIG. 2.



Analytical balance.

the centre of gravity of the beam can be raised or lowered slightly. The conditions for delicate working of a balance are as follows :

First, the two arms of the beam—that is, its length from the point of support (fulcrum) to either of the edges of support of the beam—should be of equal length and weight.

Second, the weight of the beam should be as small as is allowable, while preserving rigidity.

Third, the centre of gravity of the beam should be as near as possible to the point of support and beneath it.

Fourth, when the pans are empty the pointer should indicate the zero of the scale.

The arms of the balance should be relatively long ; length increases delicacy.

A balance is said to be *delicate* when a very small difference between the weights in the pans causes a perceptible deflection of the pointer.

The weight of a substance in air, as usually stated, is its

apparent weight. When weight is to be determined with great accuracy, the operation is carried out *in vacuo*, in order to avoid the buoyant effect of the atmosphere (see Baroscope, p. 51). This is known as *absolute weight.*

Molecular Attraction and Repulsion.—Just as the masses of matter, whether large or small, are influenced by the power of gravitation, so the molecules which make up the mass are held together with greater or less firmness by the force of molecular attraction. The intensity of this force determines also the physical state of the matter concerned. In solids the power of molecular attraction is most strongly exerted, in liquids it is weaker, and in gases it seems to be overcome by a force of repulsion which tends to separate the molecules.

We distinguish in ordinary usage between the terms *cohesion*, where molecules of like composition are held together, as the particles of iron in a bar of that metal, and *adhesion*, where bodies of unlike composition are held together, as when a glass rod is dipped into water, the force of adhesion causes the liquid to adhere to the solid.

Chemical Attraction.—The attraction between atoms which causes them to unite in the formation of molecules is otherwise known as chemical affinity, and will be referred to later (see p. 149).

7. Kinds of Molecular Attraction.

Motion may be translatory (straight or rectilinear), oscillatory, rotary, centrifugal, and centripetal.

Translatory Motion is that described by a body in moving from one place to another in a free path. If in a straight line, the motion is rectilinear ; if in a curved line, like that of a cannon-ball, it is called curvilinear motion. The best example of absolute rectilinear motion is that offered by falling bodies responding to the force of gravitation.

Laws of Falling Bodies.—When bodies starting from a state of rest are allowed to fall without resistance (*in vacuo*), they comply with three laws :

1. All bodies fall equally fast.

Since bodies fall in consequence of the earth's attraction upon each of their particles, it would follow that all bodies, regardless of size, would fall equally fast. The fact that a piece of metal falls more rapidly than a feather is solely due to the unequal resistance offered by the air. This is especially manifest with

the feather, which is usually driven from its rectilinear course. If we remove this resistance by placing the bodies in a tube which has been exhausted of air, they will then fall equally fast. Therefore the velocity of falling bodies can be correctly measured only in a vacuum.

2. The distances traversed are proportional to the squares of the times occupied in falling.

The space which a body falling *in vacuo* traverses is about 16.1 feet at the end of the first second. This varies slightly in different latitudes owing to differences of gravity (see p. 21). For example, it is at

Cape of Good Hope . . .	latitude 33° 55′ S.	= 16.070 feet.
New York	" 40° 43′ N.	= 16.079 "
Hammerfest	" 70° 40′ N.	= 16.118 "

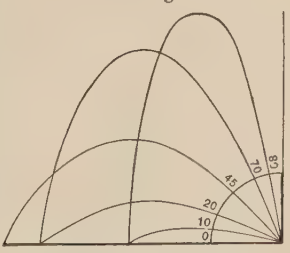
To ascertain the space traversed by a falling body during any given number of seconds, we multiply the space traversed during the first second (16.1 feet) by the square of the number of seconds. Thus, if a body falls for three seconds, it will have traversed 9×16.1 feet, or 144.9 feet.

3. The velocities acquired during the fall are proportional to the times occupied in falling.

If a body falls from a state of rest it will constantly gain in velocity, and this will, at the *end* of the first second, be at the rate of about 32.2 feet per second. This factor is known as the *acceleration* of gravity. The velocity at the end of the third second will be 3×32.2, or 96.6 feet; its average velocity for any given time will be one-half its final velocity.

Trajectory of Projectiles.—Any body thrown into the air is a projectile. When thrown obliquely the object describes a curve, called a parabola, and, according to the angle of elevation, this curve and the distance traversed vary. The greatest range or horizontal distance is attained with an elevation of 45°. The range is the same for elevations equally above or below 45°,—as 20° and 70° (see Fig. 3).

FIG. 3.



Trajectory of projectile.

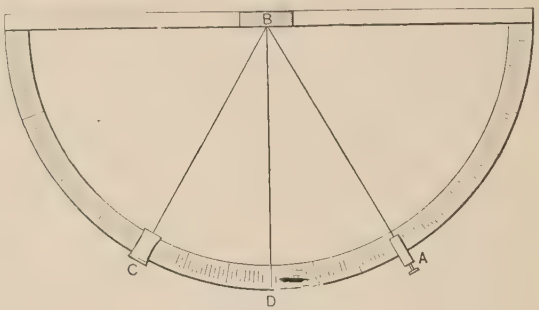
Momentum.—The momentum of a moving body is the product of its weight (mass) and its velocity. The momentum of a 50-pound cannon-ball moving at the rate

of 500 feet per second would be $50 \times 500 = 25{,}000$. The gain in momentum by a falling body weighing, for example, 150 pounds, would be as follows :

Time of fall.	Distance traversed.	Velocity.	Momentum.
First second	16.1 feet.	32.2 feet.	4,830.
Second second . .	64.4 "	64.4 "	9,600.
Third second . . .	144.9 "	96.6 "	14,490.

Reflected Motion.—When an elastic body is thrown against a hard, smooth surface, reaction causes it to rebound ; if it

FIG. 4.



Reflected motion.

strikes the surface perpendicularly, it rebounds back over the same path ; if it strikes obliquely (*the line of incidence*, A B, Fig. 4), it will be reflected back (*line of reflection*, B C, Fig. 4) in an opposite direction. The angle (A, B, D) described between the line of incidence and the perpendicular to the surface is called the angle of incidence, and the angle described between the line of reflection and the perpendicular is the angle of reflection. The law is, *the angle of reflection is equal to the angle of incidence*. This law is applicable to the reflection of sound and light.

OSCILLATORY MOTION.—While translatory motion is continuous in direction, oscillatory (vibratory) is alternate, such as is observed in the motions of a swinging pendulum, the movement of the balance-wheel of a watch, or of a sounding tuning-fork.

The Pendulum.—A pendulum is a weight (bob) suspended from a horizontal axis. If a leaden ball be suspended by a fine thread of about 3½ feet in length, it will nearly beat seconds of time in its oscillations. If, while beating, the thread be caught half-way between the point of suspension and weight, the oscillations will be more rapid, this increasing as we shorten the

length of the thread, so that the shorter the pendulum the more rapid is its oscillation. Upon restoring this pendulum to motion again with full length of string, and noting the time required to make an oscillation, we will find that so long as the amplitude of oscillation (that is, the length of the arc through which it beats) does not exceed 5°, the time of beat is invariably the same (isochronal). If the pendulum bob be drawn aside from its state of equilibrium, the force of gravity tends to draw it back, and, upon releasing, it falls to its lowest position; however, in consequence of its inertia and acquired velocity, it does not stop, but moves on in the opposite direction, forming an arc of a circle. By virtue of its new position the weight possesses potential energy, and again swings back over the same course.

We have learned that the degree of attraction of the earth varies in different latitudes, and that this same attractive force is the cause of the oscillation of the pendulum; hence the length of a pendulum beating seconds of time must vary in different latitudes,—that is, a seconds pendulum in New York must be lengthened as we proceed towards the poles, and shortened as the equator is approached. If the earth were a true sphere a given body would be equally attracted anywhere upon its surface, but owing to its flattened condition at the poles (the polar diameter being about 43 kilometers less than the equatorial diameter), these polar regions are nearer to the centre of of gravity than the equatorial; hence attraction at the equator is somewhat less than at the poles. Also, in consequence of the earth's rapid rotation, a certain portion of this force of attraction is employed in retaining the body upon its surface; otherwise it would be deflected off in consequence of centrifugal motion. The combined effect of these two causes—flattening at the poles and centrifugal force—lessens the attraction of gravitation at the equator to the extent of about $\frac{1}{192}$ part of its value at the poles.

The length of the seconds pendulum being known, the acceleration of gravity can readily be calculated; the relationship may be seen in the following table:

	Latitude.	Length of Pendulum.	Acceleration of Gravity.	
Cape of Good Hope	33° 55′ S.	39.0780 in.	32.1404 ft.	9.7962 meters.
Madras	13° 4′ N.	39.0268 "	32.0992 "	9.7836 "
New York	40° 43′ N.	39.1012 "	32.1594 "	9.8019 "
Greenwich	51° 29′ N.	39.1398 "	32.1912 "	9.8115 "
Hammerfest	70° 40′ N.	39.1948 "	32.2364 "	9.8258 "

Compensating Pendulum.—Owing to the effect of heat and cold in causing metals to expand or contract, a compensating arrangement must be provided for in the pendulums of accurate time-keepers; otherwise, owing to their expansion or contraction, they will require constant readjustment.* This may be provided for by using two different metals attached in such a way that the downward expansion of one will be exactly counteracted by the upward expansion of the other, thus keeping the length of the pendulum always the same. Another form consists in employing a tall jar of mercury supported in a stirrup as the pendulum bob. As the pendulum rod expands and lowers the centre of oscillation, the mercury by its upward expansion in the jar raises it, and the equilibrium is maintained.

Centrifugal and Centripetal Forces (Motions).—*Centrifugal* force is simply a manifestation of inertia, and signifies flying from a centre of motion. If a weight attached to a string be whirled about the hand it has a continual tendency to fly off in a straight line. This tendency is also seen in mud flying off from a rapidly revolving carriage-wheel. So great is this centrifugal force that not infrequently grindstones and fly-wheels, when their rate of revolution is very rapid, are torn asunder and the parts thrown about with destructive violence. Owing to this force, in the construction of the sharp curves in a circus, race-course, or railroad, the outside track is raised higher than the inside, so that the moving object is inclined inward. In consequence of this the weight and centrifugal force are perpendicular to the path.

Centripetal force is that which resists centrifugal, and means moving towards the centre of motion. The attraction of gravity which draws all bodies towards the earth's centre is an example of centripetal force; this prevents the centrifugal force, resulting from the earth's rapid rotation, from ejecting bodies into space. As already stated (see p. 27), centrifugal force causes a lessening in the attraction of gravity (weight) at the equator; for here this force is greatest, since the velocity of the earth's rotation is greatest. But as we approach either of the poles it grows feebler. The flattening of the earth at the poles is the effect of centrifugal motion. It is the attraction or centripetal force of the sun that retains the earth in its orbit.

* A rise of about 15° C. causes a lengthening of about $\frac{1}{4}$ millimeter ($\frac{1}{100}$ inch) of a common pendulum, and this will cause the clock to err about 10 seconds in 24 hours.

If a sponge full of water be attached to a string and rapidly whirled about, centrifugal action throws off the water, leaving it almost dry. This principle is practically applied in the *centrifuge*, which consists of a drum-like, perforated receptacle made to revolve upon an axis. Into this is placed the material to be dried, and then the centrifuge is caused to revolve at the rate of from 1200 to 2500 revolutions a minute. All fluids are thereby forcibly ejected. In this manner the adhering wash-water may be removed in the preparation of absorbent cotton, the uncrystallizable molasses from sugar, and the mother liquor from crystallized chemicals. This same principle is employed in the centrifugal clothes-wringer. Precipitation in fluids may be greatly facilitated by placing them in test-tubes and rotating rapidly in a centrifuge.

CHAPTER II.

SPECIAL PROPERTIES OF MATTER.

A. Special Properties of Solids.

It is obvious from the definition of solids as contrasted with liquids and gases (see p. 15) that they must have properties which are distinctive, and are not shared in any notable degree by the other forms of matter.

Hardness is the resistance to wearing by friction, such as scratching or rubbing, shown by a solid. It is possessed in the highest degree by the diamond, which is, therefore, capable of scratching any other solid.* Hard bodies are often used as polishing powders, as diamond dust, emery, pumice, and tripoli. Great hardness may be imparted to steel and other bodies by a process called tempering, that is, cooling them suddenly from a high temperature. Under these circumstances, however, they usually become more brittle.

Brittleness is inability to withstand compression or a blow, and indicates a want of tenacity or cohesive power between the particles of the solid. It may accompany great hardness, as in the diamond and glass.

Tenacity is the resistance to a tearing or pulling strain exerted upon solids. It may vary in different directions in the same body, as in the case of wood, where it is greater in the direction of the fibres than transversely to them. Closely connected with this are two properties chiefly shown in metals, viz., ductility and malleability.

Ductility is the capability of being drawn out into wires or threads, and is possessed especially by certain metals, like gold, platinum, iron, and copper. Glass and waxes when hot can also be drawn out into fine threads.

* The hardness of a body is expressed by referring it to a scale of hardness; that usually adopted is,

1. Talc.
2. Rock-salt.
3. Calc-spar.
4. Fluor-spar.
5. Apatite.
6. Felspar.
7. Quartz.
8. Topaz.
9. Corundum.
10. Diamond.

Malleability is the property by virtue of which bodies are flattened into thin sheets or films under the influence of hammering or rolling. It is possessed especially by metals, such as gold and copper. Lead and tin, while very malleable, possess very little ductility.

Elasticity has already been spoken of as a general property of matter (see p. 16) shared by solids, liquids, and gases, although in unequal degrees. The elasticity there referred to was, however, the elasticity of compression, and was regarded as the complement of the general property of compressibility. Elasticity of traction, or that developed by a stretching force, elasticity of torsion, or that developed by a twisting force, and elasticity of flexure, or that developed by a bending force or weight, are other phases of elasticity peculiarly belonging to solids. A familiar application of the elasticity of torsion is the torsion balance now used extensively in practice, and of the elasticity of flexure, steel springs, as for watches, carriage springs, etc.

Structure of Solids.—A solid is distinguished from a liquid or gas by possessing definite shape independent of the containing vessel. When we come to examine more closely the structure of solids, we observe notable differences. Certain substances, for instance, on passing from the liquid to the solid condition, assume characteristic shapes, as alum, nitre, sugar, ice, etc., while others become solid without assuming distinctive shapes, as fats, waxes, and flocculent and gelatinous precipitates. The former are called crystalline bodies and the latter amorphous. Again, crystalline bodies have differences of structure, due to cleavage, as in mica, rock-salt, etc., or to confused crystallization, as in granular minerals like marble, emery, etc. The several systems under which all crystalline bodies may be classified will be referred to later (see under Heat).

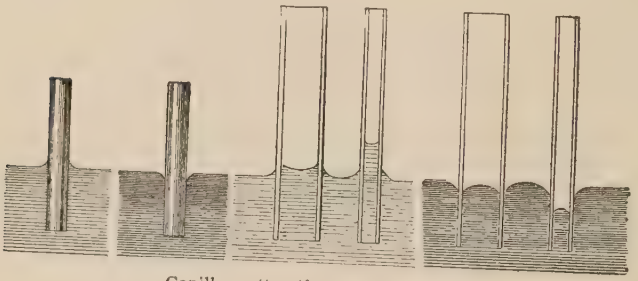
B. Special Properties of Liquids.

1. Attraction and Repulsion in Liquids.

Capillary Phenomena.—We have already referred to the adhesion of liquids to solids in speaking of the moistening of a rod of glass with water, as illustrative of the force of adhesion (see p. 24). Not all liquids show this attraction. Some even show a repulsion of the solid, as when a glass rod is dipped into mercury. Instead of a curving upward of the surface of the liquid on all sides of the glass rod, as with water, a depression of the surface occurs immediately around the rod, showing that repul-

sion exists between the mercury and the glass. The water is drawn upward around the rod because its adhesion to the glass distinctly exceeds the cohesion of the liquid; the mercury adheres to glass much less strongly than it coheres, and hence it curves away from the rod. These attractions and repulsions have an interesting illustration in the phenomena known as *capillary*, observed when tubes of relatively fine diameter are dipped into liquids. If a glass tube be dipped into a liquid which wets it (or adheres), as in the case of water, the liquid will rise in the tube to a higher level than the surrounding surface, and the height is the greater the smaller the diameter. If, on the other hand, the tube be dipped into a liquid which does not

FIG. 5.



Capillary attraction and repulsion.

wet it (or adhere), as in the case of mercury, the liquid will be depressed in the tube below the surrounding surface, and the smaller the diameter of the tube the greater the depression. These phenomena of rods and tubes are illustrated in Fig. 5. Many natural phenomena, such as the rise of moisture in rootlets and stems of plants, the rise of oil in a lamp-wick, the absorption of water by filter paper or sponges, are to be considered as illustrations of the principle of capillarity.

Diffusion of Liquids.—Closely connected with capillary phenomena are those of diffusion. If two liquids of different densities, but capable of admixture, be placed one above the other in the same vessel, they will begin to mix or diffuse through each other, even if the upper liquid be of less density than the lower. This will also take place though they be separated by porous partitions of various materials. But it is found that the rate of diffusion differs greatly for different substances. Many solids when in solution will diffuse rapidly, while others will diffuse with great slowness. The former class will be found to include

most crystallizable solids, like salt, sugar, magnesium sulphate, etc., while the latter class includes uncrystallizable or amorphous substances, like starch, gums, gelatin, or glue. To the former class the term *crystalloids* has been given, and to the latter the term *colloids* (from the Greek word for glue).

Graham founded upon this property of unequal diffusibility the process of *dialysis*. A sheet of bladder or parchment paper is stretched tightly over the lower end of an open cylinder or inverted glass funnel. The mixture of liquids to be separated by dialysis is poured in above, and the dialyser supported with the lower end immersed in pure water contained in a larger outer vessel. The crystalloid substances will diffuse through the membrane, and be found in solution in the outer vessel, while the colloids will remain in the inner vessel, or dialyser. The chemist has thus separated the crystalline arsenous acid from the colloid food material with which it may have been mixed in the stomach, and obtained it in a pure state for verification in cases of suspected poisoning.

2. Pressure of Liquids.

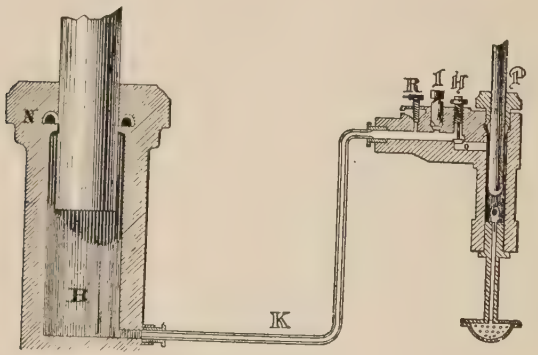
Liquids are but slightly compressible, and with the removal of the force causing pressure recover immediately their original volume. For this reason and because of the ease with which their molecules are free to move, they readily transmit pressure throughout their entire mass. This pressure is transmitted throughout the liquid equally in all directions, whether it is that in which the force is applied or at an angle to it.

This is illustrated in the case of the sprinkling nozzle of a garden hose, or similar apparatus, where the water is seen to issue with equal force from all the apertures. Of course, if the pressure in the one case is exerted over a larger area of surface than in the other, a different total force is felt in consequence. Here we must multiply the intensity of the pressure per unit of surface by the area of surface to get the total force exerted. Hence a pressure of five pounds per square inch exerted over a surface of sixteen square inches would be felt as a pressure of eighty pounds upon that surface.

An important application of this principle of transmission of pressure, and exertion of the same over a larger surface than that where it was applied, is found in the hydraulic press. This, as shown in Fig. 6, consists of a small force-pump, in which works a solid piston, P. When this piston is depressed by means of a

lever the valve *o* in the bottom of the cylinder is closed and the water is forced over through the connecting tube, K, into the larger cylinder, B. Here the pressure of the water upon the piston is exerted over an area perhaps a hundred times greater

FIG. 6.



Hydraulic press.

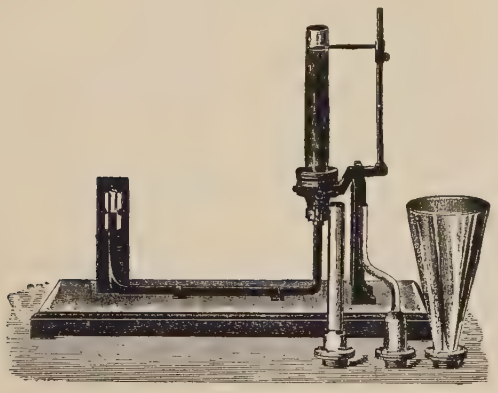
than that of the piston of the small pump, and hence the pressure is multiplied a hundred-fold. It must be remembered, however, that in our definition of energy and statement of the law of the conservation of energy (see p. 20) we said that energy could not be created any more than it could be destroyed. So in the hydraulic press, the energy developed in the larger cylinder is only seemingly greater than that exerted in the smaller cylinder. Though the pressure on the larger piston is one hundred times that applied to the smaller piston the former moves through $\frac{1}{100}$ of a foot while the latter moves through one foot. The hydraulic press is of great value in compressing cotton, hay, and other loose but bulky material, and in lifting heavy weights or moving machinery.

Vertical Downward Pressure.—In considering the pressure exerted throughout the body of a liquid we have so far disregarded the weight of the liquid itself. It is obvious that the weight of the upper layers of the liquid bears upon the layers immediately under them, and that the bottom layer therefore supports considerable weight. But because of the perfect mobility of the liquid molecules and the equal transmission of pressure in all directions, this pressure will be felt equally in all parts of the same horizontal layer, on the sides of the containing

vessel, as well as upward and downward from that level. When the depth from the surface of the liquid is twice as great, the intensity of the pressure will be twice as great, and so for different depths.

This pressure is entirely independent of the shape of the vessel containing the liquid. The diameter may be large or small without affecting the pressure, and in this way arises the seeming contradiction often called the *hydrostatic paradox*. A small body of water may exert as great a pressure upon the bottom of the containing vessel as a much larger body of water, if the height of the liquid is the same in the two cases. This

FIG. 7.



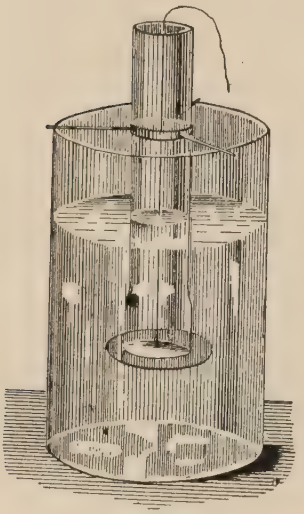
Pressure on bottom of vessels.

is true, although the two bodies of liquid may weigh differently because of the difference in amount. This may be illustrated (Fig. 7) by means of a wide **U**-shaped tube, to the upper right arm of which can be fitted tubes of various sizes and shapes. The lower tube is filled with mercury until it reaches a point indicated near the top of the left extremity. If a tube of any given diameter is attached to the right arm and filled to a certain height with water (indicated by a movable needle), the weight of this will force the mercury column up a certain distance. If this tube of water is substituted by others, the bottom diameter and height of the column being the same, the pressure exerted will be identical, irrespective of the shape of the vessel and the quantity of water it may hold.

Vertical Upward Pressure.—That the pressure in any hori-

zontal layer of a liquid is exerted equally upward as well as downward or laterally is an important fact, and is capable of a simple demonstration. If, as in Fig. 8, we take a glass cylinder, open at both ends (an Argand lamp chimney with one end ground perfectly flat will do), and, closing one end with an accurately fitting glass or metal plate, lower it into a vessel filled with water, we find that the plate is held in position by the upward pressure. Water may then be poured into the glass cylinder until the level inside nearly or quite equals the level outside, when, the upward pressure having been compensated for, the plate will drop off, because of its weight.

FIG. 8.



Upward pressure.

Lateral Pressure.—This is the pressure exerted upon the sides of the containing vessel, and is equal to the weight of a column of liquid which has a given portion or the entire side for its base, and whose height is the vertical distance from the centre of gravity of that portion to the surface of the liquid. In view of this, it is better to construct tanks for water with a considerable area of bottom and moderate height, so as to relieve the sides of the great pressure.

Equilibrium of Liquids.—As every molecule in the body of a liquid is free to move, it is obvious that the force of gravity will act upon all parts of the liquid equally, and the liquid will come to rest only when each part of the liquid is in a position of stable equilibrium. This is attained when the surface of the liquid assumes a position at right angles to the perpendicular or line in which the force of gravity is felt. We call the position so assumed a horizontal line, and the surface of a liquid free to respond to this force therefore will always be horizontal, no matter what the shape of the containing vessel. The level in several communicating vessels will also speedily become the same, as equality of pressure soon establishes itself throughout the entire body of liquid, and the several surfaces come to rest in the same horizontal plane.

Just as the plumb-line is a practical device for quickly and easily determining the perpendicular line, so we have in the spirit-level a ready means of determining whether a surface is perfectly horizontal. It consists of a glass tube nearly filled with alcohol, a bubble of air only remaining. When this tube is mounted in a wooden or metal case, and the latter placed upon a horizontal surface, the air-bubble shows exactly in the middle of the upper surface of the tube, upon which a scale is marked. If the surface upon which the level is placed is not perfectly horizontal, the bubble moves towards one end or the other of the scale instead of remaining in the middle.

The Artesian well is an illustration of the principle of the equilibrium of liquids. In this case the strata which hold the water are shut in above and below by impervious layers of clay. At the same time, the water here accumulated has worked its way down from a much higher level. When the upper clay layer is perforated in sinking the well, the water rises, tending to reach the level from which it started.

3. Pressure upon Bodies Immersed in Liquids.

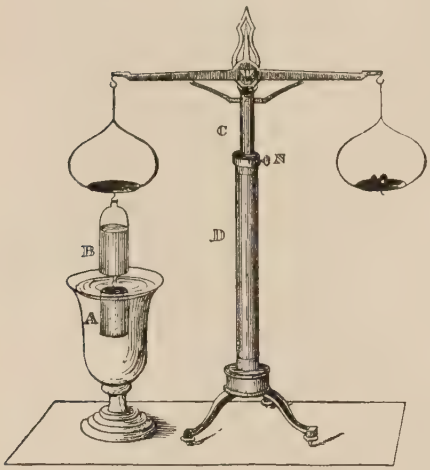
We have seen that the pressure felt upon any molecule within the body of a liquid varies with the depth and is exerted equally upward as well as downward. We are now prepared to consider the effect of this pressure upon a solid body immersed in the liquid. As the horizontal pressures act from all sides, they may be considered as neutralizing each other. We have, therefore, only the pressures in a vertical direction to consider. It is obvious that upon the top of the solid there is exerted a vertical downward pressure, measured by the depth of this horizontal layer from the surface of the liquid, while against the under surface of the solid there is a vertical upward pressure, measured by the depth of that horizontal layer from the surface of the liquid. Of course, the pressure in the lower horizontal layer will be greater. Hence the solid will be pushed upward by a pressure greater than that which bears upon its upper surface, and greater by the weight of a column of the liquid equal in height to the difference in depth between the top and the bottom of the solid.

This result for the case of a body immersed in water is, therefore, expressed by saying that the excess of upward pressure *is equal to the weight of the volume of water displaced by the immersed body.*

This excess of upward pressure (or *buoyancy*, as it is termed)

obviously has its effect temporarily upon the weight of the solid body. The weight may be totally or partially overcome by this buoyancy, as the preceding considerations show us that *a body immersed in a liquid loses a part of its weight equal to the weight of the displaced liquid.* This statement may be very exactly demonstrated by the hydrostatic balance, as shown in Fig. 9. The solid brass cylinder A fits exactly in the brass cup B. The two are hooked together, suspended from the one pan of a balance, and counter-balanced exactly by weights placed in the other pan. A glass globe, or other vessel, is now placed in position around the brass cylinder, and water poured in gradually. The buoyant effect of the water causes the cylinder A to rise, so that the two pans of the balance no longer show equilibrium. If, however, water is poured into the brass cup B, the cylinder sinks, and when the cup has been filled, it will be found that the cylinder is just immersed, and that the two sides of the balance are exactly in equilibrium. Obviously the brass cylinder lost a portion of its weight exactly equal to the weight of an equal volume of water. This so-called principle of Archimedes gives us a convenient means of determining the volume of any solid which is not soluble in water. By weighing the solid first in air and then when immersed in water, we arrive at the weight of the equal volume of water displaced, and, as the relations of weight and volume of water are known (1 cubic centimeter of water at 4° C. weighing 1 gramme), we get the volume of the body which displaced the water.

FIG. 9.



Hydrostatic balance.

Its most important application, however, is in determining the relative weight of different solids and liquids, or, as it is termed, their *specific gravity* or density. The density or specific gravity of a body represents the relative degree of closeness of the particles which make up its mass (see p. 17). In order to

ascertain this, comparison is made between the weight of a given volume of the body and an equal volume of some standard. For solids and fluids, distilled water (at either 4° or 15.5° C.) is selected; for gases, hydrogen or pure air. We say the specific gravity of iron is 7.5; this means that it is 7.5 times denser than water. The density of ether is 0.725,—that is, where a certain volume of water weighs 1000 grammes, the same volume of ether would weigh 725 grammes; it is, therefore, lighter than water.

For Solids.—Weigh the body in air, then weigh again when immersed in water, and the weight in air divided by the loss of weight when weighed in water will give the specific gravity.

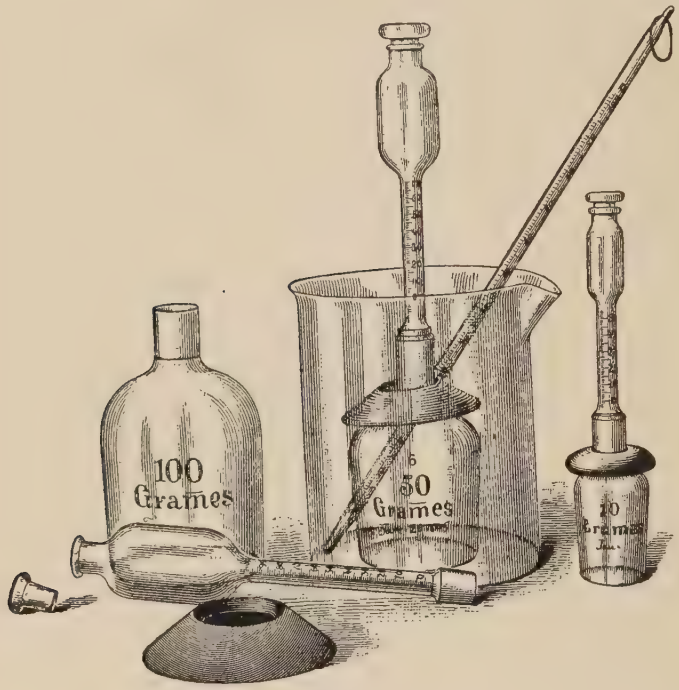
In carrying out the specific gravity determinations of solids practically we have several methods to choose from. We may use the specific gravity balance, in which case the solid is suspended from one arm of the balance by a hair, or silken filament, and weighed first in air and then immersed in a small cup of water supported independently of the balance-pan and not touching it. Or, for powdered solids, the specific gravity flask may conveniently be used. This is a small glass-stoppered bottle, the weight of which, both empty and filled with distilled water, has been determined. For greater accuracy the ground-glass stopper is perforated, so that in fitting it to the bottle any excess of water may be forced out and wiped off with a piece of soft paper. In making a determination, the bottle is carefully dried, and, the powder having been placed in it, is weighed. This gives the weight of the solid in air. The bottle is then filled up with water, the excess being wiped from the top of the stopper, and weighed. The weight found is that of the powder, the bottle, and the original volume of water minus what has been displaced by the powder, which, of course, gives us the weight needed for the specific gravity calculation. In this determination by the aid of the specific gravity bottle, the water must be boiled previously, to expel the air, or the bottle, after filling in the powder and water, be put under an air-pump and exhausted.

A form of specific gravity bottle for very accurate work is that devised by Dr. Squibb and illustrated in Fig. 10. The bottle is weighted by means of a leaden collar, and the graduation on the stem allows of its being adjusted with great accuracy.

In the case of solids soluble in water, some other liquid, like naphtha or oil of turpentine, the specific gravity of which is

already known, may be used. The solid is weighed in air and then immersed in the liquid chosen and the weight again taken. We are thus able to determine its specific gravity with reference to the liquid chosen. If the known specific gravity of this liquid based upon water be then multiplied by the specific gravity found, we will have the true specific gravity of the solid based upon water.

FIG. 10.



Apparatus for specific gravity, according to Dr. Squibb.

For Liquids.—The specific gravity or density of liquids is usually ascertained by means of the specific gravity bottle. The exact weight capacity of these in distilled water is indicated on the outside. This is usually an even quantity, as 100, 50, 25, or 10 grammes. All that is necessary, then, is to fill the bottle up to the indicated mark with the liquid to be examined, and divide this by the weight capacity of the bottle. Thus, a bottle which holds, when filled, exactly 100 grammes of distilled water (at 15.5° C.), will, when filled with glycerin at the same tem-

perature, weigh 125 grammes ; with alcohol, 82 grammes ; hence their specific gravities would be $\frac{125}{100} = 1.25$, and $\frac{82}{100} = 0.820$.

In practice specific gravity is more conveniently determined by the aid of what are termed *hydrometers*. These are glass tubes loaded at the lower end with mercury or shot, so that they will float upright when immersed in a liquid. On the stem is marked a scale of degrees or equal parts. It is obvious that if one of these hydrometers sink to a certain depth in water, it will sink still deeper in a liquid lighter than water, or float higher in one heavier than water. If then the point to which it sinks in water be marked 1 of the scale, the distance above this would be marked in decimal fractions less than 1, while the distance below would be marked in fractions greater than 1. In order to mark slight differences more accurately, a number of hydrometers are used in a set, of which several are weighted and graduated for liquids lighter than water and several for liquids heavier than water. Arbitrary scales are also in use for hydrometers, such as that of Baumé for liquids heavier than water, that of Baumé for liquids lighter than water, and those of Tralles, Twaddle, Gay-Lussac, Beck, etc. Special forms for particular liquids are also used, as alcoholometers, salimeters, saccharometers, lactometers, etc.

For Gases.—The preceding principles are applicable here. However, owing to the great variations which the volumes of gases undergo from slight changes in temperature and barometric pressure, a number of corrections are necessary, for which see works on Advanced Physics. Briefly stated, a large, light glass globe, after exhausting of air and noting its weight, is filled with the gas to be examined and weighed, temperature and barometric pressure being noted. This is again exhausted and filled either with pure dry air or hydrogen gas, and weighed under exactly the same conditions. The density is then ascertained by dividing the weight of the given volume of the gas by that of the same volume of hydrogen or air. All weights are reduced to the pressure of 760 millimeters and temperature of 0° C.

C. General Properties of Gases.

1. Attraction and Repulsion in Gases.

Physical Properties.—As already stated, a gas is an aërial medium in which the repellent forces are superior to the co-

hesive among its molecules ; hence gases tend to expand and diffuse unless confined. They are therefore distinguished from liquids by this tendency of indefinite expansion. The molecules of gases are in a constant state of activity, flying about in every conceivable direction, constantly colliding with one another with enormous velocities. As a result, gases exert a pressure (tension*) equal in all directions, which increases with the decrease of their confined space.

Since heat acts as a repellent force among molecules, the volume of gases will necessarily be subject to temperature changes,—that is, expanding or contracting regularly with an increase or decrease of temperature (see Law of Charles, p. 67). Likewise, the volume of a gas readily responds to an increase or decrease of pressure. This expansive force of gaseous bodies may be illustrated by placing a small rubber balloon partially distended with air or gas, but securely closed to prevent the escape of the gas, under the receiver of an air-pump (see p. 51). Upon exhausting the air from within the receiver, the balloon immediately distends and swells to several times its original bulk. This is, of course, due to the expansion of the gas under diminished pressure, as when the air is admitted again to the receiver of the pump the balloon contracts to its original dimensions.

The law governing this change of volume under changing pressure is known as *Mariotte's law*, or, sometimes, *Boyle's law*, and is thus expressed. *The temperature remaining the same, the volume of a given quantity of a gas is inversely as the pressure it bears, also its density and tension (elastic force)*,—that is, the less the pressure the greater the volume, and the greater the pressure the less the volume. Thus, if the pressure on a confined volume of a gas be *doubled*, its volume will be reduced *one-half*, and, as a consequence of this, the density (degree of closeness of its molecules) and tension (elastic force) of the gas will be doubled. In other words, the greater the tension the greater is the elastic force and the smaller the volume of the gas. It should be noted, however, that there are limits to this contraction in volume under the influence of pressure. Every gas, when sufficiently cooled, will at some definite pressure assume a liquid condition. No amount of pressure at any point above this temperature will cause liquefaction.

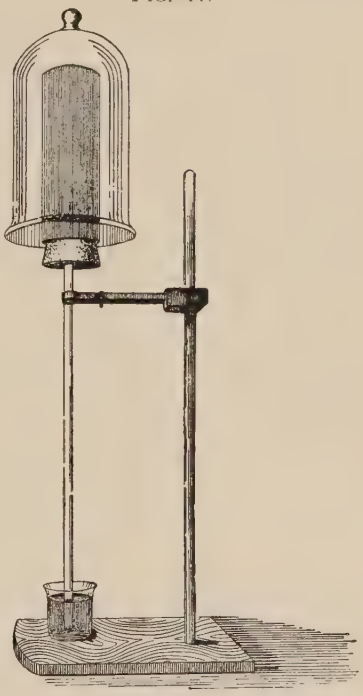
* The term *tension* as employed here means "elastic force" or "pressure."

This temperature of liquefaction is called the *critical temperature*. The pressure exerted by a gas at the critical temperature (at which it would condense at once if the temperature were lowered) is known as the *critical pressure*.*

Owing to the great variations in volume produced by temperature and pressure, all calculations and comparisons are reduced to a *standard temperature* of 0° C. and *pressure* of 760 millimeters.

Diffusion of Gases.—Gases possess the power of diffusing, whereby two gases of different densities rapidly become a homogeneous mixture, in the highest degree, as might be expected from the freedom of motion possessed by their molecules. Porous diaphragms of parchment, rubber, or unglazed pottery all allow of this diffusion. It may be illustrated by the apparatus shown in Fig. 11. In this case, the porous cell shown fitted to the upright glass tube is filled with air, while a bell-jar containing hydrogen is held for a moment depressed around it. Gaseous diffusion immediately takes place through the walls of the porous cup, and the result is a mixture of hydrogen and air, both within and without the porous dividing wall. But hydrogen, as the lighter gas, diffuses more rapidly than the air, and the result is an excess of

FIG. 11.



Diffusion of gases.

* CRITICAL TEMPERATURES AND PRESSURES.

	Critical Temperature.	Critical Pressure.
Sulphur dioxide	155.4° C.	78.9 atmospheres
Ammonia	130.0° C.	115.0 "
Carbon dioxide	30.92° C.	73.0 "
Nitrogen	—146.00° C.	35.0 "
Oxygen	—119.00° C.	51.0 "

the gaseous mixture within the cup, and, in consequence, a bubbling out at the bottom of the upright glass tube.

The rapidity of diffusion of two gases of different densities is *inversely as the square root of the densities of the gases.* Thus, as hydrogen is about 14.5 times lighter than air, it will diffuse nearly four times faster than air.

*Density of Gases and Vapors.**—The density of a gas or vapor is the amount of matter contained in the unit of volume. For ascertaining this relative density, see p. 38. Gases and vapors are collected, according to their density, either over fluids or by displacement. (1) *Collection over fluids:* a jar or tube is filled with water and then inverted in a trough of water, keeping its mouth just below the surface. The gas, escaping from a generator, is allowed to bubble upward, displacing the water. Such relative light gases as hydrogen, oxygen, nitrogen, marsh gas, and carbon monoxide are thus collected. Soluble vapors, as those of ammonia and hydrochloric acid, are collected over mercury. However, these can be collected by (2) *Displacement:* this consists either in introducing the gas by a tube into the bottom of the jar, the entering gas displacing the air, when it is called *downward displacement*, or in passing the gas up to the top of an inverted jar, when it is called *upward displacement.* The height to which the vessel is filled may be judged in some cases by the color of the gas (as chlorine and nitrogen trioxide), in others by means of chemical tests, as the extinguishing of a lighted taper (as carbon dioxide, sulphur dioxide, ammonia). Carbon dioxide is so heavy that it can readily be poured from one vessel into another.

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* Vapors are aëriform bodies which can readily be made to assume the liquid state by a moderate reduction of temperature or by means of slight pressure. As examples we have ammonia, the gaseous halogen acids, sulphur trioxide, nitrogen tri- or tetra-oxide.

RELATIVE DENSITY OF GASES.

	Air as 1.	Hydrogen as 1. Oxygen as 15.96.
Air	1.000	14.44
Oxygen	1.105	15.96
Nitrogen	0.971	14.02
Hydrogen	0.069	1.00
Carbon dioxide	1.530	22.08
Carbon monoxide	0.954	13.78
Marsh gas	0.562	8.11
Chlorine	2.422	34.98
Sulphur dioxide	2.115	30.54
Ammonia	0.595	8.60

Absorption of Gases by Liquids and Solids.—The solubility of gases in water* conforms to the following laws :

1. *The quantity of gas absorbed decreases with the rise of temperature,*—that is, as the temperature is lowered the amount of gas absorbed increases. For example, 1 volume of water dissolves 1 volume of carbon dioxide at 14° C.; at 0° C. it takes up 1.8 volumes. 1 volume of water dissolves 730 volumes of ammonia at 15° C. and 1050 volumes at 0° C. On raising the temperature of such solutions the excess of gas passes off.

2. *The quantity of gas dissolved increases or decreases with the pressure* (the temperature remaining the same). Thus, at the temperature of 14° C., 1 volume of water absorbs 1 volume of carbon dioxide under the pressure of 1 atmosphere ; under 2 atmospheres, 2 volumes of the gas ; under 3 atmospheres, 3 volumes. A solution of 5 volumes, under 5 atmospheres, is called "soda water." On removing this pressure the excess of gas escapes.

3. *The quantity of a gas which a liquid can dissolve is independent of the nature and quantity of other gases which it already holds in solution.* Thus, when air—a mixture of 1 part of oxygen and 4 parts of nitrogen—is dissolved in water, each of the gases is absorbed in the same proportion as though each were alone present,—namely, 1 to 1.87,—that is, a saturated aqueous solution of oxygen will take up nitrogen (or any other gas) as readily as though the former were not present.

Numerous examples of the solubility of gases will be found in the discussion of the chemical elements.

It will be noted that vapors—as ammonia, sulphur dioxide, hydrochloric acid gas, etc., which are more easily liquefied—are far more soluble in water than the true gases.

The absorption of gases by solids is considered to be due to the attraction, which causes the gases to deposit in a more or less thick layer of condensed gas upon the surface of the solid. Porous bodies which expose an immensely increased surface in proportion to their size readily absorb gases ; for example, fresh wood charcoal will absorb ninety times its volume of am-

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* At the temperature of 0° C., and pressure of 760 millimeters, one volume of water dissolves of

Nitrogen	0.020 vol.	Sulphur dioxide	79.80 vol.
Oxygen	0.041 "	Ammonia gas	505.00 "
Carbonic oxide	1.800 "	Hydrochloric acid gas	1150.00 "
Sulphuretted hydrogen	4.37 "		

monia gas, 55 volumes of sulphuretted hydrogen, and so on. This explains the disinfecting power of charcoal.

Occlusion.—Certain metals, like silver or palladium, possess the power of taking up or occluding many times their volume of certain gases; for example, melted silver absorbs about twenty-two times its volume of oxygen from the air. This is expelled on cooling. At 100° C. palladium will absorb about 650 volumes of hydrogen. Platinum, in the form of powder (platinum black, or sponge), possesses high absorbent power; it will, for example, condense upon its surface two hundred and fifty times its volume of oxygen. Advantage is frequently taken of this, in order to bring about chemical combination between gaseous elements (see p. 165).

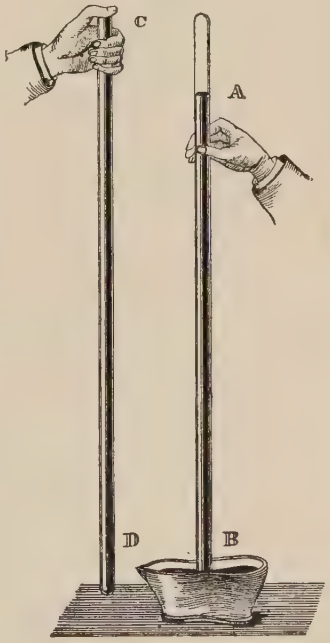
2. Atmospheric Pressure.

The Atmosphere and its Pressure.—The atmosphere is an aërial envelope that surrounds the earth; it is held by the attraction of gravity, and attends the earth in its rotation. At the equator the velocity of the earth is over one thousand miles an hour, at the poles it is nil. There are constant local disturbances in this gaseous ocean, which are chiefly due to changes in temperature, and, as a result, winds are produced which reestablish this equilibrium. Since the atmosphere possesses weight, it consequently exerts a pressure upon all bodies. This pressure decreases as we ascend. The *downward pressure* may be simply illustrated by means of the leather sucker, which consists of a circular piece of thick, wet leather, through the centre of which a stout string is tied. This disk is then securely pressed against a flat object, removing all air from the under surface. A heavy object may thus be raised, since the downward pressure of the atmosphere binds the leather securely to the weight. The *upward pressure* can be demonstrated by filling a tumbler with water and covering with a piece of cardboard. Care should be taken that no air is admitted under the card. The card is held in position until the tumbler has been inverted, then, on removing the hand, the water will remain in the inverted glass, being held there by the upward air pressure. That the atmosphere *presses equally in all directions* may be illustrated by the Magdeburg hemispheres, which consist of two metallic hemispheres, the edges of which have been accurately ground. When placed together a hollow sphere is formed, which can be exhausted of air through the stem of one of the hemispheres,

which is provided with a stop-cock. After exhausting the air from the interior by means of an air-pump, the stop-cock is closed, and it will then be found that, on account of the equal pressure of the atmosphere in all directions upon the sphere, only by the exertion of a force greater than this pressure can the two hemispheres be separated.

These experiments show that the atmosphere presses upon everything upon the earth's surface with a weight which must be quite considerable. How much this pressure measures was first shown in the experiment of Torricelli. This is illustrated in Fig. 12. A glass tube about a meter long and sealed at one end is filled with mercury. Having closed the open end of the tube with the thumb, the tube is inverted and dipped into a small vessel filled with mercury. The column of mercury is seen to fall, and after some slight oscillation remains stationary at about thirty inches (760 millimeters) above the level of the mercury in the outer vessel. No matter how long the tube may be, or what its diameter, this height of the mercury column is always observed. Only one explanation of this fact is possible. It is that the atmospheric pressure will support a column of mercury some thirty inches (760 millimeters) in height and no more. The space above the mercury in the inverted tube is a vacuum, and hence there is no counterbalancing pressure upon the mercury at this point. If the upper or closed end of the tube be provided with a stop-cock and air be admitted, the mercury in the tube will immediately fall and come to the same level as that in the outer vessel.

FIG. 12.



Torricellian tube and vacuum.

When water is used instead of mercury, it is found that the atmospheric pressure will support a column thirty-four feet in height, which is about 13.6 times as high as the mercury column. But mercury is 13.6 times heavier than

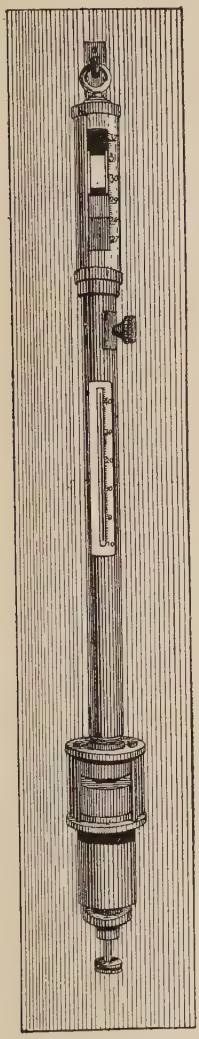
water, so that the weight of the two columns is the same in the two cases, and is supported by the exertion of the same pressure. To reduce this to a simple numerical expression, let us assume that the area of the tube in the experiment with mercury is a square inch. We thus have thirty cubic inches of mercury supported by the pressure of the atmosphere. A cubic inch of mercury weighs 3433.5 grains, or 0.49 of a pound, so that the weight of the thirty inches is 14.7 pounds. It is customary to consider the atmospheric pressure as equalling in round numbers fifteen pounds upon a square inch of surface, and this is often referred to as a pressure of one atmosphere. The instruments used for measuring atmospheric pressure are called

Barometers.—The simplest form of barometer, of course, is the straight tube of Torricelli, as just described. This tube, suitably mounted in a frame on which a scale has been constructed and dipping into a small cup filled with mercury, constitutes the cistern barometer. A small opening is made in the cistern (Fig. 13) to allow the air access to the mercury. Another form, preferred for many purposes, is the siphon barometer, shown in Fig. 14. In this case the tube has two unequal branches, of which the longer is closed, and the shorter, acting as the cistern, has an opening (Fig. 14) communicating with the air. There are two scales, one at either end, so as to note the height of the mercury in either branch. The distance between the upper and lower levels (Fig. 14) constitutes the barometric column. In order that the instrument may be inclined for transportation, a very fine calibrated tube connects the two columns, which prevents any air from penetrating into the longer arm. At the sea-level this is almost exactly thirty inches of the English scale, or 760 millimeters of the metric scale. At any considerable height above the sea-level, of course, the pressure is less, because the lower layers of the atmosphere have been passed, and, as these layers are denser than those above them, the barometric reading will be notably less. Thus, at a height of 3.4 miles, or 17,952 feet (the height of some of the Alpine peaks), exactly one-half of the atmospheric pressure is felt, as indicated by the barometer reading of fifteen inches.

Still another form of barometer (Figs. 15 and 16), and the one most generally used by travellers in determining the height of mountains, on account of its lightness and portable character, is the *aneroid barometer*. This is a flat, thin-walled, circular box of corrugated metal, partially exhausted of air and then her-

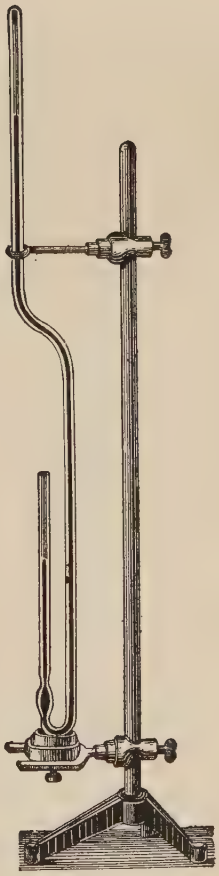
metically sealed. The variations of the atmospheric pressure upon the top of this box cause a system of levers to register by means of a needle running over a graduated dial face. The

FIG. 13.



Cistern barometer.

FIG. 14.



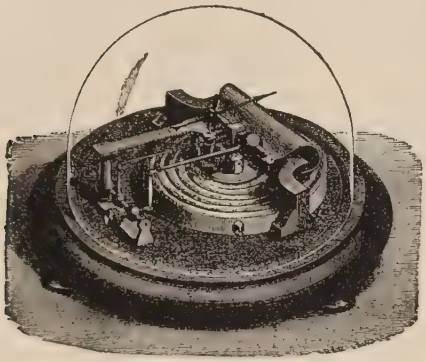
Siphon barometer.

graduation must, of course, be made by comparison with a standard mercurial barometer.

Barometric variations are usually opposite to those of the

thermometer,—that is, when the former rises the latter falls, and *vice versa*. The barometer indicates changes in the density and weight of the air caused by its expansion or contraction. Such changes, attended by a rise in the barometer, indicate conditions which do not favor precipitation of moisture, while a fall

Fig. 15.



Aneroid barometer, mechanism.

Fig. 16.

Aneroid barometer.

in the column indicates precipitation.* A rise or fall of the mercury does not necessarily indicate fair weather or rain, for such conditions are largely influenced by the degree of humidity and the direction and force of the prevalent winds. Slight variations of the barometer take place daily.

3. Buoyancy of Gases.

The principle of Archimedes (see p. 38), whereby a body immersed in a liquid loses a portion of its weight equal to the weight of the displaced liquid, is equally true of gases, and that they possess buoyancy or supporting power upon bodies immersed in them is easily shown. A small scale-beam is taken, capable of being put under the bell-jar of an air-pump, and from one arm of this a hollow sphere is suspended, counterbalanced

* The indications usually recorded on the dial face of barometers are as follows:

31	inches,	787 millimeters	. . . . . Very dry.
30⅔	"	779 "	. . . . . Settled weather.
30⅓	"	770.7 "	. . . . . Fine weather.
30	"	762 "	. . . . . Variable.
29⅔	"	753 "	. . . . . Rain or wind.
29⅓	"	744.7 "	. . . . . Much rain.
29	"	736 "	. . . . . Tempestuous.

by a small weight attached to the other arm. When this is put under the bell-jar and the air exhausted, the hollow sphere, deprived of the buoyant effect of the air, sinks and appears to be heavier than the small weight, which feels the buoyant effect of the air much less because of its smaller bulk. The apparatus employed for illustrating this phenomenon is called the baroscope (Fig. 17). Owing to this buoyant effect of the air, very accurate weighings are made in a vacuum (see p. 24).

Fig. 17.

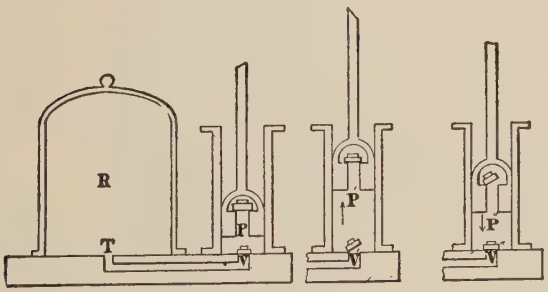
Baroscope.

An important application of the buoyancy of the air is the use of balloons. These are simply hollow spheres of light but impermeable material, such as silk coated with caoutchouc or other varnish, which enclose a large volume of some light gas, like hydrogen or illuminating gas, and displace a corresponding volume of air. The weight of the balloon and its equipment, together with that of the volume of gas contained, subtracted from the weight of the volume of air displaced, will give the ascensional force of the balloon.

4. Apparatus based upon Atmospheric Pressure.

The Air-Pump.—The exhaustion from any given space of the air contained, or the removal of the atmospheric pressure, not only is important as allowing us to demonstrate the effects of

Fig. 18.

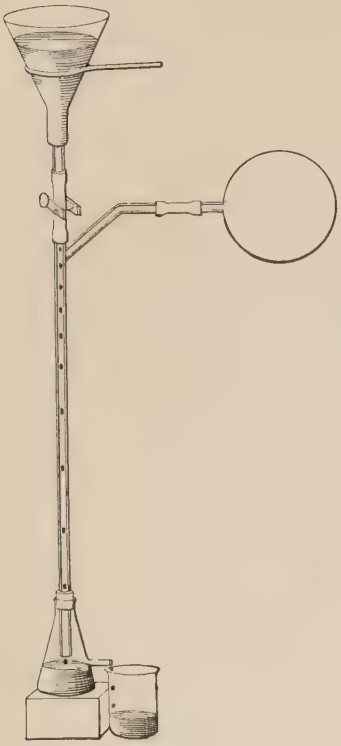


Air-pump.

this pressure, but is a necessary operation in many manufacturing processes, as in evaporation of liquids *in vacuo*, the exhaustion of globes for incandescent electric lamps, operating the condensers of steam-engines, etc. We will here refer only,

however, to the portable forms of exhausting pumps for production of a vacuum. Fig. 18 gives a sectional view of the common form of air-pump. If we start with the piston P at the bottom of the cylinder, as it is drawn up the valve V′ opens upward and air is drawn out of the receiver R. When the piston begins to descend, the valve V″ closes and the valve in piston P″ opens, letting the air escape into the space above the piston. The air can thus be considerably rarefied by a few strokes, but it is impossible to produce a perfect vacuum, owing to the difficulty of securing perfectly fitting joints for the apparatus.

FIG. 19.



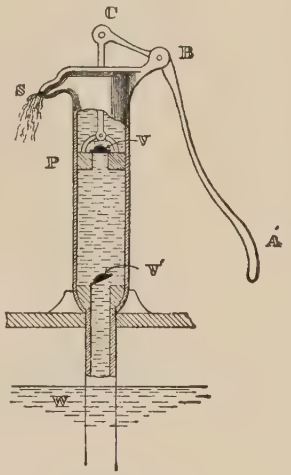
Mercury pump.

A more perfect vacuum is attained by the aid of the Sprengel mercury pump. A simplified form is shown in Fig. 19. The Bunsen filter pump, which is much used in chemical and pharmaceutical laboratories, is constructed upon this same principle. It is attached to the water-tap, and water is forced through under considerable pressure. As high a degree of vacuum is not attainable with this as with the mercury pump. This consists simply of a vertical tube of narrow bore, something over a yard in height, a few inches from the top of which a lateral tube is made to connect perfectly air-tight. If now mercury be poured into the vertical tube by the aid of a funnel, in falling it draws the air from the vessel connected with the lateral tube until a complete vacuum has been established therein, when a column of mercury thirty inches in height will stand in the vertical tube. These pumps are used exclusively in producing the vacuum needed for incandescent electric-light globes.

Condensing Pumps.—By a different arrangement of the valves in the cylinder and side-tube, instead of exhausting a given space,

additional air may be forced in and so brought under considerable pressure. Compressed air has many applications as a substitute for steam ; also in tunnelling, laying of submarine caissons, air-brakes, in conjunction with air-pumps, in operating pneumatic mail tubes, etc. A condensing pump is also useful in condensing other gases than air, as in forcing carbon dioxide under pressure into solutions.

FIG. 20.



Lifting pump.

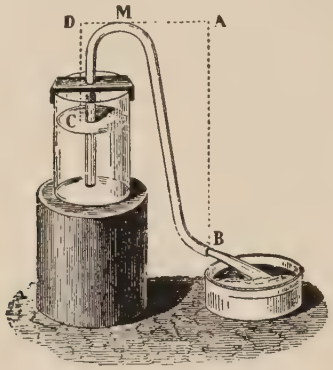
Lifting and Suction Pumps.—An important application of the principle of atmospheric pressure is seen in the pumps devised for the lifting of water from wells and cisterns. One of the common forms is illustrated in Fig. 20. The action here exactly corresponds to that in the cylinder of the air-pump. As the piston P is drawn up, the valve V′, known as a clack-valve, opens upward, and air with water following it is drawn up into the cylinder. As the piston descends, the valve V′ closes and V opens. After a few strokes the water is lifted by this action from the depth W to the cylinder and there remains, filling the whole length of the tube. It is obvious that the action of the piston first exhausts the cylinder of air, and that the water rises into the vacuum thus formed, where it remains unless the leakage of air into the cylinder causes the water to fall again to the level of that below. Other forms of pumps combine the principle of exhaustion and pressure, and thus can deliver a continuous stream of water.

The Siphon.—This is simply a tube bent at an acute angle, open at both ends, and with legs of unequal length. If the siphon be filled with liquid and the longer end closed temporarily, on dipping the shorter leg into the liquid contained in an open vessel a flow begins when the longer leg of tube is unstopped, and the liquid will drain from the vessel until the level falls below the end of the short leg. The explanation of the action of the siphon is simple, and is readily had from a consideration of Fig. 21.

The continuous flow is caused by the difference in pressure at C and at B. The pressure at C is the atmospheric pressure

minus a column of liquid, C D ; while at B it is the atmospheric pressure minus A B. And as this latter pressure is less than the other, the force acting on the surface of the liquid at C drives

FIG. 21.



Siphon.

the water out. The flow, moreover, is more rapid the greater the difference in level between the two ends of the siphon.

CHAPTER III.

ACOUSTICS.

1. Vibrations and Undulations.

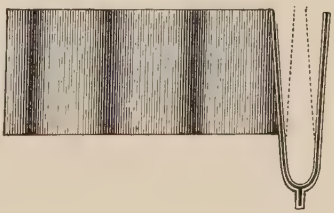
Acoustics treats of the laws of generation, propagation, and comparison of sound.

Sound originates with vibrations of elastic matter. These vibrations excite undulations in the air, whereby they are communicated to the ear.

Vibrations.—All sounding bodies vibrate. These vibrations are oscillatory movements, like the swinging to and fro of the prongs of a sounding tuning-fork.

Undulations or Sound-Waves.—Vibrations are communicated to the ear by means of undulations or sound-waves in the air. Just as a pebble dropping upon the surface of still water produces wave-like rings due to vertical undulations, a vibratory body produces by its rapid backward and forward movement alternate condensed and rarefied air stratas, which represent waves. Fig. 22 represents the formation of these sound-waves, as above described, while by means of an attached needle and drawing a vibrating fork over the surface of smoked glass the wave-motion described by these movements may be recorded, as shown in Fig. 23.

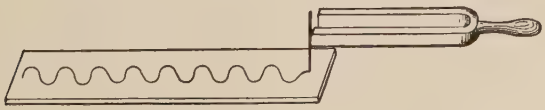
FIG. 22.



Vibrations with wave production.

The length of a sound-wave is the distance from the middle of one condensation to the middle of the next,—that is, from one wave-crest to the next

FIG. 23.



Sound-waves.

crest. This represents one complete to-and-fro movement of the vibrating body. The height of a sound-wave, or the dis-

tance from the middle point to either of its extreme positions, is known as its *amplitude*.

2. General Properties of Sound.

A musical sound consists of harmonic motion,—that is, it is the result of a succession of vibrations at equal intervals and of sufficient rapidity. The human ear is limited in its range of hearing of musical sounds. The low limit is about 16 vibrations, while the higher is about 38,000 per second. These extremes produce notes so low and acutely high that they are not appreciable to many: the average limits are usually placed from 40 to 5000 per second. The highest note produced by the piccolo is 4752 vibrations per second.

Propagation of Sound.—For the propagation of sound an elastic medium like the air is absolutely necessary. This is proved by suspending a bell in a glass globe from which the air has been removed by means of an air-pump. As the exhaustion proceeds the sound of the bell grows feebler, until it ceases altogether. Sound may be propagated to a great distance through the air. Cannonading has been heard fifty or more miles under favorable conditions. Sound travels still farther and more distinctly through the earth's surface; instances have been recorded in which it has been carried a distance of 370 miles.

Velocity of Sound.—That it requires an appreciable time for sound to travel from point to point may be seen in the difference of time elapsing between the flash of a distant gun and the report, or between the blows of a hammer and the time the sounds reach the ear. Experiments have shown that at 0° C. (32° F.) the velocity of sound is about 333 meters, or 1090 feet, per second. This increases about one foot per second for every degree Fahrenheit, and two feet for every degree Celsius. Since an English mile is about 1609 meters, sound requires about 4¾ seconds to traverse the distance. Sound travels more rapidly in liquids and solids, owing to their greater elasticity. Thus,—

In *water*, sound travels about 4 times as fast as in air.
" *lead*, " " " 4 " " " "
" *wood*, " " " 10–18 " " " "
" *steel*, " " " 16 " " " "
" *glass*, " " " 16 " " " "

Speaking-Tubes.—Sound-waves are propagated in every direction in open spaces, hence rapidly lose in intensity at a

distance. However, on speaking into a trumpet (megaphone) or speaking-tube, the sound-waves are condensed and carried a long distance. The ear-trumpet employed by deaf persons is a reversed speaking-trumpet; it serves to collect and concentrate the sound-waves. Based on this same principle is the *stethoscope*, an instrument used by physicians for locating sounds in the human body. This consists of a small, wide funnel made of metal or hard rubber, to the neck of which is attached rubber tubes, which can be adjusted to the ear. By means of this instrument feeble sounds are condensed and accurately transmitted.

Echoes and Resonance.—An *echo* is a reflected sound. When the distance of the reflecting surface is very short, the sound is strengthened and gives rise to *resonance*. A tuning-fork which has been struck sounds very much louder when the handle is placed on a box or is held in front of its open end. The same effect will be produced if held over the mouth of a wide tube closed at one end, or a cylinder. These are called resonant tubes or boxes, and the cause of their reinforcing effect is that the confined column of air vibrates sympathetically with the sounding object. This principle is employed in the construction of such musical instruments as the violin, zither, and piano; also the resonance of columns of air is the chief source of sound in wind instruments, as flutes, horns, organ-pipes. The openings in the flute and the valves in the horn regulate the length of the column of resonant air, while the pitch of the organ-pipe depends on its length. In those instruments based upon the vibration of cords or wires, as the violin, harp, or piano, the pitch of tone is governed by the number of vibrations, which, in turn, are controlled by the tension, length, size, and density of the cords. These conditions are formulated as laws:

1. *The number of vibrations is inversely as the length of the cord.* Thus, if a given cord makes 18 vibrations per second, it will make 36 (an octave higher) if its length be reduced one-half, or 54 when reduced one-third.

2. *The pitch varies as the square root of the tension.* If the tension of a cord which gives a certain note be quadrupled, it will render a note an octave higher.

3. *The pitch varies inversely as the diameter.* Small cords vibrate more rapidly than large ones, hence render more acute sounds. A cord of any given size will give twice as many vibrations (an octave higher) as one double its size.

4. *The pitch varies inversely as the square root of the density.* The denser the cord the slower the vibrations and the graver the notes.

3. Special Properties of Sound.

As regards their effect upon the sense of hearing, sounds differ from one another in three essential particulars,—their intensity, pitch, and timbre.

Intensity or *loudness* depends on the extent of the vibrations. This may be illustrated by striking a certain chord on the piano or harp,—first softly, and then with considerable force. In the latter case a much louder sound is produced, although the note is exactly the same. This difference is due to the greater amplitude of vibration,—that is, the amount of displacement of the vibrating body, which increases with the force with which it has been struck. Intensity of sound, therefore, depends upon the amplitude or extent of vibration.

Pitch.—The pitch of a tone or its position on the musical scale depends upon the number of vibrations per second of the sounding body. For shrill notes the vibrations are short and very rapid, for low notes they are long and slow. For example, the pitch of the note C_3 is about two hundred and fifty-six vibrations a second.

Timbre or *quality* are terms which distinguish the same note or pitch of tone as produced on different instruments. Thus, the same note sounded on a violin, piano, and organ is produced by the same number of vibrations per second, yet each of the three notes possesses distinct characteristic qualities by which it may be identified,—that is, their timbre is different. A chord or any sounding body vibrates as a whole, producing its fundamental or primary tone ; at the same time, it vibrates in equal parts or segments, giving rise to secondary or higher tones, more usually known as overtones. The blending of these determines the quality or character of the sound.

4. Transmission of Sound Vibrations.

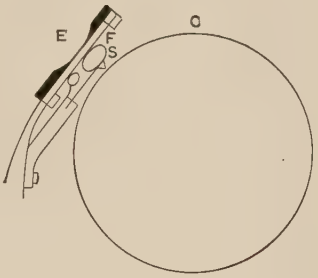
Sound-waves impinging against an elastic membrane cause it to vibrate in unison. This vibrating medium is, in turn, able to reproduce the sound received. Based on this general principle are the phonograph and telephone * In order to obtain a clearer

* The consideration of the telephone belongs more properly under the subject of electro-magnetism (see p. 141).

understanding of the former, the principle of the string telephone will first be considered. This consists of two tin cups or cylinders ; over one end of each is stretched an elastic membrane (bladder or parchment). Through a pin-hole in the middle of each is secured a cord (any length up to one thousand feet), knotted at both ends and kept taut. When speaking into the open end of one of the cups, its membrane is caused to vibrate from the action of the sound-waves. These vibrations are transmitted by the connecting cord to the membrane of the other cup, where they are reproduced as sounds.

The Phonograph.—This consists of a mouth-piece, E (Fig. 24), at the base of which is a thin metallic disk, F, which is thrown into vibration when the operator speaks. Resting against this disk is a rounded knob, S, tipped with a small steel point, which plays upon the rotating cylinder, C, transferring the vibrations of the disk as a series of indentations upon a wax surface, which correspond exactly with the number of vibrations the needle makes. If the cylinder be turned round, so as to permit the needle to pass over these indentations, it will cause the point and with it the metallic disk to be thrown into the same number and kind of vibrations, reproducing identically the same sounds it had received.

FIG. 24.



Section of phonograph.

CHAPTER IV.

RADIANT ENERGY.—I. Heat.

I. The Nature of Heat.

Heat is a form of energy due to molecular vibration. This vibration seems to be taking place in greater or less degree in all bodies, and, when communicated to the ether which fills all space around the vibrating body, is transmitted to the nerves of sensation, and so is felt as heat. The presence of air is not essential for this transmission of heat vibrations, as they are transmitted equally in vacuo as in air. When these vibrations become more rapid the heated body may become luminous, and this manifestation of radiant energy is called light. Electrical energy seems to be due to vibrations of the same nature, but of still greater rapidity of movement. Such is the undulatory or vibratory theory of heat and light. The fact that one of these related forms of energy can be changed readily into the others, and that all of them can be produced from mechanical energy, renders this theory a very probable explanation of the observed phenomena.

II. Sources of Heat.

1. Physical Sources.—It is to solar radiation absorbed and transformed that we owe primarily all the various manifestations of energy that take place on our planet. It is the energy of sunlight that sustains all forms of life and supplies us with food and fuel. According to Helmholtz, the earth receives only $\frac{1}{2300000000}$ part of the whole solar radiation, and the source of the sun's heat is its slow contraction in volume, its density being one-quarter that of the earth. A shrinkage equivalent to $\frac{1}{10000}$ its diameter would evolve heat sufficient for 2100 years.

The earth possesses also a heat of its own, readily noted as we descend to any considerable depth below its surface, and made evident to us in hot springs and volcanoes. The explanation most generally accepted for this is that the earth has cooled from a much more highly heated state, probably that of an incandes-

cent gas, and that, while a hard crust has formed upon the surface, the interior of the globe is yet in a molten and liquid state.

2. Chemical Sources.—Most forms of chemical combination, as we will see later, are accompanied by the development of heat in definite amounts, or are *exothermic*. Hence every case of combustion going on about us in nature contributes to the development of heat. This includes the rapid combustion of all forms of fuel, and the slow combustion or decay of organic matter. It includes also the respiration of all kinds of animals, and the processes of assimilation of food equally due to chemical and heat-producing changes. Those forms of fuel which are richest in the elements carbon and hydrogen possess the greatest value as fuel, as by the oxidation of these elements the maximum of heat can be developed. Hence the value for heating purposes of the several varieties of coal, of petroleum, of hydrocarbon gases, and of so-called "water-gas."

3. Mechanical Sources.—Friction and percussion are among the commonest of the methods by which heat is developed. The old device of obtaining sparks from a piece of flint and a steel, and the still older one of the savage of rubbing together two dry sticks to kindle a fire, are illustrations of the development of heat by friction. The "hot-box" on a railway car, where the heat developed by the friction of the car-axle in its box often suffices to ignite the oil-soaked waste, is also an illustration. The striking of the blacksmith's hammer upon the anvil readily illustrates the heat developed by percussion. In this case the energy of the mass of the hammer in descending is changed when it strikes into the molecular energy of the particles known and recognizable by the senses as heat.

Mechanical Equivalent of Heat.—The fact that visible mechanical or mass motion may be changed into molecular motion, or heat, suggests that a mechanical equivalent may be established for a given development of heat. This idea, first brought forward by Mayer, was experimentally established by Joule. He determined the number of foot-pounds (see p. 19) of energy equivalent to a unit quantity of heat. He used a copper vessel filled with water and provided with brass paddle-wheels, which were set in motion by the falling of weights. The weights being known and the space through which they fell, as well as the difference in temperature of the water at the beginning and at the end of the fall, the amount of fall corresponding to an increase of one degree was readily calculated. The result expressed in

English units is that to raise one pound of water one degree Fahrenheit requires 772 foot-pounds, or to develop one degree Centigrade requires 1390 foot-pounds.

III. Effects of Heat.

If we refer for a moment to the explanation given as to the nature of heat, we can conjecture what the effects of the application of heat to a body would necessarily be. In the first place, the vibrations already existing between the molecules or particles of the body will be increased in rapidity, and the body, to use the common expression, becomes hotter. This is made evident by rise of temperature, appreciable by the senses or by more accurate recording instruments. In the second place, these vibrations will increase not only in rapidity but in amplitude, and the body expands, the force of cohesion having been weakened while that of repulsion tends more strongly to drive the molecules apart. In the third place, this loss of cohesive power may go so far that change of physical condition results. A solid body under the influence of heat may fuse or liquefy, and a liquid when heated may boil and be entirely volatilized. We shall take up these several effects of heat in succession for more detailed study.

1. Rise of Temperature.—This is the first and most general effect of heat. Indeed, it might be called the invariable effect except for the case which will be referred to later, when the heat applied is consumed in doing the work of changing the physical condition of the body, or, as it has been termed, is rendered *latent*. In this case it does not show in the raising of the temperature of the body (see p. 69).

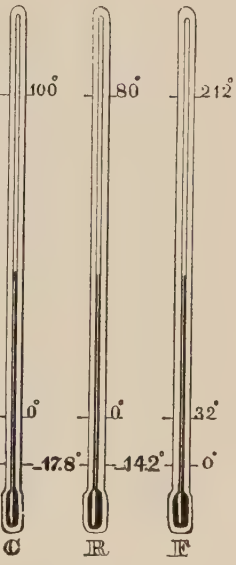
Rise of temperature is in some cases appreciable by the senses, but more delicate means of distinguishing are clearly obtainable in the use of what are termed *thermometers*, or heat-measurers. These usually depend upon the expansion and contraction under the influence of heat and cold of a liquid or gas, but the expansion and contraction of metals are also availed of at times.

The ordinary thermometer is that in which mercury is used. It consists of a glass bulb of spherical or cylindrical shape connected with a fine capillary tube or stem. The bulb and part of the stem having been filled with mercury, this is boiled to expel the air and the tube is sealed up. To establish a scale for the thermometer when thus filled, two fixed points are needed. One is obtained by immersing the bulb in melting ice, and the other by

suspending it in steam from water boiling at normal pressure, and these points are permanently marked upon the glass. Between these two a scale is now to be made and the individual divisions or degrees of the scale are to be marked.

Three scales have been proposed and are now in more or less common use. The Fahrenheit (used commonly in England and in the United States), the Réaumur (the domestic thermometer of Germany, Sweden, and Denmark), and the Centigrade or Celsius (used generally in Europe, but more particularly in scientific literature). The two fixed points before referred to serve equally for all of these, but the method of dividing the space between the two points is different in each of them. The distinction between the several scales is shown in Fig. 25. In the Centigrade and the Réaumur scales the lower fixed point (the melting point of ice) is called zero, while in the Fahrenheit scale it is put at the 32d division of a scale which starts lower. The upper fixed point (the boiling point of water) is taken as 100 degrees of the Centigrade scale, as 80 degrees of the Réaumur scale, and as 212 degrees of the Fahrenheit scale. Consequently, the space between the two fixed points is divided into 100 degrees in the Centigrade scale, into 80 degrees in the Réaumur scale, and into 180 degrees in the Fahrenheit scale. Divisions of the same value are continued both above and below the fixed points upon each of the several scales, degrees below zero being indicated by the sign minus. One degree of the Centigrade scale (expressed 1° C.) will equal $\frac{4}{5}$ of a degree Réaumur (1° R.) and $\frac{9}{5}$ of a degree Fahrenheit (1° F.).

FIG. 25.



Comparison of thermometer scales.

The conversion of readings of the Centigrade scale into the corresponding readings of the Réaumur scale, and *vice versa*, is easily effected by the aid of this fraction, using the expressions C.° $\times \frac{4}{5}$ = R.°, and R.° $\times \frac{5}{4}$ = C.°.

In the case of the Fahrenheit scale the problem is not quite so simple, as the zero of this scale does not agree with that of the other two, and instead of the lower fixed point of the scale being

placed at zero it is 32 degrees above zero. This inequality is easily overcome, however, and to convert Fahrenheit readings into Centigrade we use the expression (F. —32) $\frac{5}{9}$ = C., and to convert Centigrade readings into Fahrenheit, $\frac{9}{5}$ C. + 32 = F. When the minus sign is prefixed to a reading, this must be taken into account in adding or subtracting the 32.

The Centigrade scale is readily seen to be the most convenient as well as the most philosophical of these several scales, and it has practically displaced the other two in all exact and scientific work.

The limits of use of the mercurial thermometer are, of course, reached as we approach the freezing or the boiling point of mercury. The lower limit of accuracy is —36° C., as mercury freezes at —40° C.; the upper limit is about 300° C., as mercury boils at 350° C.

Mercury thermometers increase their readings with age, and during the first year after their manufacture this increase amounts to as much as one degree or more. Very accurate thermometers are filled at least two years before graduating. A thermometer is said to be *delicate* when it indicates very small differences of temperature. This depends on the ratio of the size of the bulb to the diameter of the capillary; for if the volume of mercury is large and the capillary small, a minute change of temperature will cause the column to rise through an appreciable distance. Thermometers are *sensitive* when they quickly assume the temperature of the surrounding medium. This depends upon the surface-area of the bulb. For this reason they should be made cylindrical, long, or coiled.

Alcohol Thermometers.—Colored alcohol is used in place of mercury for such thermometers as are employed in recording extremely low temperatures. Alcohol solidifies at —100° C. and boils at 78° C.

Metallic Thermometers.—These dial thermometers are in common use, and consist of a double strip composed of steel and brass riveted together, usually bent into the form of a coil. The inside extremity is secured to the back of the instrument, while the other movable extremity is attached to the needle of the dial. Owing to the unequal expansion and contraction of the two metals, the coil closes or opens, moving the dial accordingly.

Air Thermometers.—These are based on the expansion or contraction of a closed volume of air. They are exceedingly

sensitive, and are used to measure very small differences of temperature. Air thermometers are employed in standardizing mercurial thermometers ; also for measuring high temperatures. They consist of a large bulb of glass, porcelain, or platinum filled with dry air, connected with an open capillary tube, which contains a small index of colored sulphuric acid, which moves along or recedes as the air expands or contracts. A millimeter scale records the volume of contraction or expansion.

Pyrometers are used for measuring extremely high temperatures. They are based on the influence of heat affecting the electrical conductivity of a heavy platinum wire. From the resistance in ohms the temperature in degrees may be calculated. Pyrometers based on the expansion of metals through heat are no longer used for recording high temperatures.

2. **Expansion.**—This is brought about through the influence of heat, which weakens the force of cohesion and causes a more rapid vibration of the molecules of a substance, whereby they tend to separate more widely.

Solids.—All solids expand more or less under the influence of heat. The extent of this expansion depends on the amplitude of vibration of the individual molecules. Expansion may be either *linear* (length) or *cubical* (volume). The increase in length of many substances caused by a rise of 1° C. has been carefully measured, and differs considerably, but is always uniform for the same substance. The rate of increase for a unit of length when its temperature rises through 1° C. is known as the *coefficient of linear expansion.* This is ascertained by making two marks on a rod of the substance, and accurately noting its length at 0° C., then at 100° C. Dividing the total expansion by the temperature change (100° C.), we have the expansion for 1° C. The quotient obtained by dividing this by the initial length is called the coefficient.* The coefficient of linear expansion multiplied by three gives that of *cubical expansion.*

We meet with numerous practical illustrations and applications of the expansion of solids. Furnace bars must not be fastened tightly into masonry at both ends, lest they split the masonry

*Coefficients of Linear Expansion of Solids between 0° and 100° C.

Pine	0.00000608	Iron	0.0000122
Marble	0.00000849	Copper	0.0000171
Glass	0.00000837	Sulphur	0.0000642
Platinum	0.00000857	Ebonite	0.0000842

by expanding ; water-pipes are provided with telescopic joints to allow of expansion ; in laying rails for railways, space must be left between two connecting rails for expansion ; iron tires are put upon wagon-wheels while highly heated, so that in contracting they may tighten all parts of the wheel ; hot liquids cannot be poured into vessels of thick glass without danger of breaking, because of the unequal expansion of the glass.

Liquids.—Owing to the slighter degree of cohesion among the molecules of liquids, they expand to a greater degree and more rapidly than solids. This expansion differs greatly with different liquids : thus, the cubical volume expansion of chloroform is ten times that of mercury.* In measuring the expansion of liquids we must distinguish between the *apparent* expansion, which is that of the liquid with its container,—which also expands,—and the *absolute* or *real* expansion of the liquid itself, irrespective of that of the containing vessel.

Water presents an important exception to the rule that liquids expand uniformly with the increase of heat and contract with cold. When water is cooled down gradually from the ordinary temperature, it contracts until 4° C. (39° F.) is reached, when it begins to expand, and continues to increase in volume until it freezes at 0° (32° F.). Hence it shows its maximum density at 4° C. This is of the greatest importance in nature. As the water in lakes and rivers cools in winter, it contracts and sinks until the temperature of 4° is reached. After this the cooler layer becomes lighter and remains on the surface, where it congeals and forms ice, which in time protects the water below from the extreme low temperature to which the air may be reduced. In this way fish and other fresh-water animals are able to live through severe winters without experiencing any lower temperature than 4° C. The expansion of water in cooling to form ice also plays a very important part in the operations of nature. More than any other force it reduces rocks to fragments by freezing in crevices and splitting off small particles. It bursts iron and leaden pipes and other vessels in which it may be when these are exposed to low temperatures.

Gases.—Since there is no coherence between the molecules of

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* Coefficients of Expansion (Apparent) of Liquids between 0° and 100° C.

Mercury	0.0154	Ether	0.064
Water	0.0466	Alcohol	0.116
Sulphuric acid	0.0600	Chloroform	0.157

a gas to be overcome, heat will cause a far greater expansion than among solids or liquids. While the rate of expansion among solids and liquids varies greatly, with all gases it is constant. Owing to the volume sensibility of gases to pressure and temperature changes, it is necessary in accurate measurements to observe certain standards for comparison. *The standard temperature is 0° Celsius, and the standard pressure 760 millimeters.* The influence of pressure is explained by the law of Mariotte (see p. 42), while that of temperature is governed by the law of Charles,*—namely, *the volume of a gas is proportional to its absolute temperature;* that is, gases expand or contract equally in volume by heat or cold. Further, this expansion or contraction is $\frac{1}{273}$ of its volume for each degree Celsius; and if it were possible to cool a gas to a temperature of —273° C., all molecular movement would cease, and a gaseous state would no longer exist. This temperature is known as *absolute zero*, which means a total absence of any degree of heat. A gas at 0° C. may be regarded as having been heated through 273° C.; a temperature of —30° C. is 243° of absolute temperature; a temperature of +30° C. is 303° of absolute temperature.

Calorimetry.—This is the process of measuring the quantity of heat absorbed or given off by substances. Of the two standards of measurement, one is called a *caloric*, which is the amount of heat required to raise one kilogramme of water through 1° Celsius; the other, a *thermal unit*, which is the quantity of heat required to raise one pound of water through 1° Celsius.

Specific Heat.—Different substances have different capacities for heat,—that is, the same weights of different substances require different quantities of heat to warm them equally. The amount of heat which will raise one gramme of water through 1° Celsius will raise the same mass of ice through 2° C., the same of iron about 11° C., and of mercury 32° C. Again, if bullets of iron, copper, tin, and lead of exactly the same weight are all heated to the same temperature in boiling water, and then quickly dropped on a disk of wax, the iron ball melts its way through first, followed by the copper and tin in order, while the lead, if the cake is not too thin, will remain embedded in the wax. From this it will be seen that the specific heat of these substances differs considerably. As standard for comparison, the specific heat of water is taken as unity, or 1; that of any other sub-

* Sometimes called Gay-Lussac's Law.

stance by comparing the quantity of heat required to raise its temperature 1° with that required to raise the temperature of the same weight of water 1°.

If we mix one kilo of water at 0° C. with one kilo of mercury at 100° C., the two bodies will interchange heat and assume a common temperature of 3.2° C. The mercury has cooled 96.8° C. (100° —3.2° C.), and given off 3.2 calories (heat units). The quantities of heat contained in these equal weights are as 96.8 to 3.2,—that is, the specific heat of the mercury (water = 1) would be $\frac{3.2}{96.8} = 0.0332$. The specific heat of all the various elements has been ascertained. This knowledge has become of great importance, in consequence of the discovery by Dulong and Petit of the law, *that the product of the specific heat of an element, and its atomic weight, is approximately a constant number*,—namely, about 6.4. This product is known as the *atomic heat* of an element.* By aid of this constant, the atomic weight of any new element may approximately be ascertained by dividing 6.4 by its specific heat $\left(\frac{6.4}{\text{Sp. Heat}} = \text{At. Wt.}\right)$. The accuracy of this result may subsequently be verified by chemical analysis.

3. Changes of Condition.—The three states of matter already described—namely, solid, liquid, and gaseous—depend upon the relations of the forces of cohesion and repulsion. Heat opposes the former, and tends to change solids to liquids or gases by increasing the rate and amplitude of vibration among the molecules. When a solid passes into a liquid state it is said to undergo

Fusion (melting or liquefaction).—Some substances are very refractory, or incapable of fusion except at excessively high temperatures ; and some—chiefly those of complex chemical composition, such as paper, wood, and vegetable and animal fibres and tissues—are decomposed without fusion. With these exceptions, we may consider fusion a regular change which solids

* A few examples are cited for illustration :

	Specific Heat.	Atomic Weight.	Atomic Heat.
Bromine	0.0843	80.	6.74
Iron	0.1138	56.	6.37
Mercury	0.0332	200.	6.64
Nickel	0.1092	58.7	6.41
Platinum	0.324	197.5	6.40
Potassium	0.1655	39.1	6.47
Tin	0.0555	118.	6.55

will undergo when the proper temperature is reached. Fusion is governed by the following laws :

1. Every substance begins to fuse at a certain temperature, which is invariable for each substance if the pressure be constant.

2. Whatever the intensity of the source of heat, from the moment fusion commences the temperature of the body ceases to rise and remains constant until the fusion is complete.

The range of temperature shown in the fusing points of solids is very great, varying from —38.8° C. for mercury to 1900° C. for platinum.

Some substances show no definite melting point, as glass and iron, which soften gradually until liquefaction is reached. Such is called *vitreous fusion.* Generally solids expand on fusing ; however, there are some exceptions, as, for example, ice, type metal, and cast iron, which contract in volume during liquefaction.

When metals are fused together they generally form a homogeneous mixture which often possesses properties quite different from those possessed by either of the metals singly. Such mixtures are called *alloys.* They are generally more fusible than either of the metals of which they are composed. For instance, Rose's fusible metal, consisting of 4 parts of bismuth, 1 part of lead, and 1 part of tin, melts at 94° C., while its most fusible constituent, tin, melts at 228° C. Wood's fusible metal, consisting of 1 or 2 parts of cadmium, 2 parts of tin, 4 parts of lead, and 7 or 8 parts of bismuth, melts between 66° and 71° C. These alloys are largely used for solders and in taking casts.

Latent Heat of Fusion.—In accordance with the second law noted above, bodies which are capable of fusion cannot be heated any higher until fusion is complete, no matter how intense the source of heat may be. If a pound of water at 80° C. be mixed with a pound of water at 0° C., the result will be two pounds of water at 40° C. But if a pound of water at 80° C. be mixed with a pound of ice at 0° C., the two pounds of water obtained will have a temperature of 0° C. The pound of ice in melting has used up the 80 degrees of heat originally possessed by the pound of water, so that this latter pound and the pound resulting from the melting of the ice are equally at 0° C. These 80 degrees of heat have disappeared as sensible heat. But, as before stated, energy cannot be destroyed. It must, therefore, still be present, although stored up as potential energy under the name of *the latent heat of fusion.* That these 80 degrees of heat have been

temporarily absorbed without raising the temperature of the water produced from the ice is capable of proof, as when the pound of water again becomes ice this absorbed heat is all given out, and can by measurement be shown to be the equal of that which disappeared before. Every liquid has its own latent heat. That of water, as established by the above experiment, is 80° C.

Dissociation. —The process of heating can be carried to such a degree that many chemical compounds are broken up into their elements. The velocity of the oscillations of the molecules and atoms increases with the temperature, and will finally reach a limit at which the atoms are no longer able to remain together. This process of separation is called dissociation. For example, water begins to dissociate into hydrogen and oxygen at about 1200° C., ammonium chloride into ammonia and hydrogen chloride gases. These molecules again reunite upon lowering the temperature.

Regelation.—When two pieces of ice are firmly pressed together they unite at the surface of contact. The pressure exerted liquefies the ice at the point of contact; but as the latent heat of fusion is absorbed and conducted away, the water is converted into ice. The formation of the snow-ball depends on regelation.

Solution of Solids in Liquids.—When brought in contact with liquids, the cohesion among the molecules of many solids is broken up, and the result is a homogeneous fluid mixture called a solution. The solubility of a solid in a fluid depends upon the nature of the solid, the temperature, and the solvent. When the latter has taken up all that it is capable of dissolving at a certain temperature, it is said to be *saturated.* The number of grammes of a substance which at a certain temperature will dissolve in 100 grammes of water is known as the *coefficient of solubility* of that substance.

As a rule, crystalline inorganic bodies dissolve more readily in water; metals in mercury (amalgams); fats, resins, oils, and organic crystalline bodies in alcohol. Increase of temperature increases the degree of solubility, with few exceptions; as, for example, calcium hydrate, sulphate, and citrate are less soluble in hot than in cold water. When two or more salts are dissolved in water without chemical action on one another, we may have one of three conditions: (*a*) the quantity of each dissolved is as great as though it alone had been used; (*b*) the total quantity of each dissolved is greater than if one alone had

been used, the addition of the second or third salt increasing the solubility of that previously added ; (*c*) the quantity of each salt held in solution is less than if it were alone present, although the sum total dissolved is greater than if only one had been used.

The freezing point of a solvent is lowered by the presence of a dissolved salt.

When the solution of a solid is attended by chemical action, a rise in temperature follows, evidenced by dissolving potassium hydrate, zinc chloride, or calcium oxide in water.

When crystalline solids are dissolved in water (as also in the case of fusion), a certain quantity of heat is absorbed or rendered latent, and the mixture becomes very cold. Advantage is taken of this in preparing

Freezing Mixtures, by means of which various degrees of cold may be produced. Thus, a mixture of two parts of powdered ice or snow and one part of salt will rapidly reduce the temperature of substances around which it may be packed. The salt forces the liquefaction of the ice, thereby lowering the temperature ; the water resulting from this dissolves the salt, again lowering the temperature ; so that their combined action produces a temperature of zero Fahrenheit.*

Solidification of Liquids.—Just as change of condition takes place when solid bodies fuse under the influence of heat or dissolve in liquids, so the reverse change may take place, whereby the liquid may resume the solid form, either from fusion or from solution. For this change the following laws, analogous to those before stated for fusion, may be given :

1. Every body under the same pressure solidifies at a fixed temperature, which is the same as that of fusion.

2. From the commencement to the end of the solidification the temperature of a liquid remains constant.

This second law, it will be seen, is the counterpart of the law of

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* The following table gives a list of salts which, when mixed with solvents, reduce temperature, owing to rapidity of liquefaction. The colder the solvent the lower will be the temperature produced.

Sodium sulphate 8 parts + hydrochloric acid 5 parts reduces from +10° C. to about −17° C.

Snow 2 parts + salt 1 part reduces from +10° C. to about −18° C.

Sodium sulphate 3 parts + dilute nitric acid 2 parts reduces from +10° C. to about −19° C.

Sodium sulphate 6 parts + ammonium nitrate 5 parts reduces from +10° C. to about −26° C.

Sodium phosphate 9 parts + dilute nitric acid 4 parts reduces from +10° C. to about −30 C.

fusion already explained involving the absorption or storing up of heat. Just as in the other case, no matter what the heat applied, the temperature of the melting solid remained constant until the operation was completed, so in this reverse change, no matter how intense the cold, the giving out of the potential heat energy stored up in the liquid prevents any lowering of the temperature until the solidification is complete.

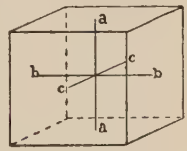
This principle of the storing up of heat in the liquefaction of a solid and giving it out in the reverse change of solidification of the liquid has a great importance in the economy of nature. The first severe cold of winter does not cause the streams and lakes to freeze up suddenly and completely, because for every pound of ice produced eighty heat units are given out and have a notable retarding influence upon the freezing operation ; similarly the first warm days of spring do not instantly melt the accumulated snow and ice of the mountain valleys, because for every pound of ice melted eighty heat units must be taken up and withdrawn from present effect upon the temperature.

It is obvious that, as the phenomena of solution are analogous to those of fusion, so we may have as the counterpart of solidification from fusion a solidification from solution. In the former case change of temperature is the occasion of the solidification ; in the latter, besides this cause, we may have the removal by evaporation or otherwise of the solvent as the determining cause of the solidification.

4. Crystallization.—Generally speaking, bodies in passing from the liquid or vaporous condition to the solid state assume regular geometric forms. Such regular forms, bounded by plane faces and definite angles, are called *crystals*. Such bodies as do not conform to the above—that is, do not crystallize—are called *amorphous* (as chalk, glue, acacia, etc.). The plane surfaces which bound a crystal are called *faces* or *planes*. The intersection of two adjacent faces (planes) forms an *edge*. When two or more lines or planes intersect, their edges form an *angle*. In order to classify and compare the various forms of crystals, we express the relative position and inclination of their planes by referring them to certain systems of axes. These axes (*a*, *b*, *c*, *d* of Figs. 26, 27, 28, 29, 30, 31) are called crystallographic axes ; they are imaginary lines, which, if drawn through, would intersect at the centre of the crystal. The positions of the different faces (planes) of the crystal are fixed by, and expressed in, the relative lengths of their intercepts on

these axes. For the purpose of comparing the different crystal planes, systems of symbols have been devised, which aim to locate the position of each plane, with reference to its relation to the crystallographic axes. Since every crystalline body has its own peculiar form, it will readily be seen that we have an immense number of these in all possible varieties. However, in the face of this, according to their greater or less degree of symmetry, they are divided into six different classes or systems. Each one of these systems has its imaginary crystallographic axis, to which the different planes (faces) bear a fixed symmetrical position. According to the relative position, number, and size of these different planes, we distinguish the following *six* different systems :

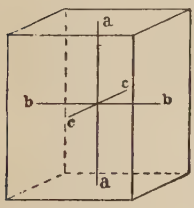
FIG. 26.



Regular system of crystallization.

1. The *Regular* (isometric, monometric) *System* (Fig. 26). All forms have *three* axes of *equal* length, which intersect at angles of 90°. To this system belong the cube and octahedron with their many modifications. In this system crystallize the diamond, the various alums, sodium chloride, potassium iodide, bromide, and chloride, etc.

FIG. 27.

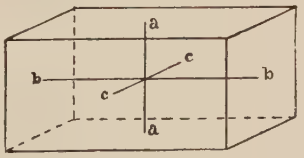


Tetragonal system of crystallization.

2. The *Tetragonal* (dimetric, quadratic) *System* (Fig. 27) has *three* axes, which intersect at angles of 90° ; two of these (lateral) being of equal length, the other (principal axis) is either longer or shorter. To this system belong the square pyramid and prism, and in it crystallize potassium ferrocyanide, tinstone, nickel sulphate, etc.

3. The *Rhombic* (orthorhombic, trimetric, prismatic) *System* (Fig. 28) has *three* axes of *unequal* length, all intersecting at right angles. To this system belong the rhombic pyramid and prism, and in it crystallize barytes, sulphur, saltpetre, zinc sulphate, citric acid, etc.

FIG. 28.



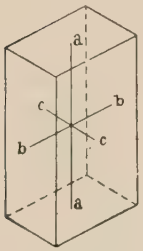
Rhombic system of crystallization.

4. The *Monoclinic* (oblique, prismatic) *System* (Fig. 29) has *three* axes of *unequal* length, two of which intersect at an oblique angle and are perpendicular to the third. To this system belong the oblique pyramid and prism, and in it crystallize oxalic acid,

tartaric acid, sodium sulphate, ferrous sulphate, sulphur (fused), etc.

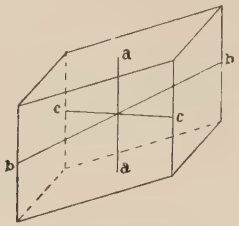
5. The *Triclinic* (asymetric) *System* (Fig. 30) has *three* axes of *unequal* length, all oblique to one another. The most common form is the doubly oblique pyramid, and in it crystallize copper sulphate, potassium dichromate, etc.

FIG. 29.



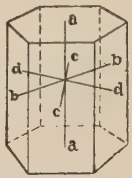
Monoclinic system of crystallization.

FIG. 30.



Triclinic system of crystallization.

FIG. 31.



Hexagonal system of crystallization.

6. The *Hexagonal System* (Fig. 31) has *four* axes; three of these, of equal length, are lateral, and intersect the principal axis at angles of 90°, and one another at angles of 60°. The principal axis may be longer or shorter than the lateral axes. To this system belong the hexagonal pyramid and prism, and in it crystallize quartz, Iceland spar, thymol, bismuth, antimony, etc.

5. Vaporization.

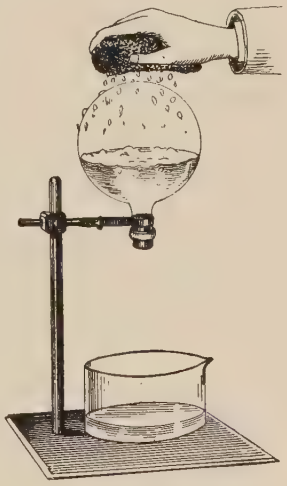
Solids.—Should the boiling point of a solid be lower than its fusing point, it will sublime when heated,—that is, it passes directly into vapor form without liquefaction. This process of sublimation is either carried out as a means of purification, as in the case of camphor, iodine, sulphur, etc., or as a synthetic process in the preparation of calomel or corrosive sublimate.

Liquids.—The conversion of a liquid into a state of vapor is designated as *vaporization.* If this vaporization takes place slowly from the surface of a liquid, it is called *evaporation*, while if the vapor is produced rapidly throughout the mass of fluid, it is termed *ebullition* (boiling). When a fluid is heated, the atmosphere resting immediately upon its surface soon becomes saturated with vapor, and as the temperature increases, the tension (elastic force) of this vapor layer gradually increases until it equals that of the atmosphere; this is the normal *ebulli-*

tion (boiling) *point* of the fluid. The laws governing ebullition are as follows :

1. *The temperature of ebullition, or the boiling point, increases with the pressure.* The influence of pressure is of far greater importance here than in the case of the fusion of a solid. This is because of the readiness with which a gas or vapor responds to difference of pressure, and of the fact that slow evaporation passes by gradual stages into rapid evaporation, or boiling. We may generalize this statement by saying that a liquid boils when the tension of its vapor is equal to or exceeds the pressure it supports. Hence, as the pressure increases or diminishes, the tension of the vapor and, therefore, the temperature necessary for boiling must increase or diminish ; it being borne in mind that the temperature of a liquid cannot be raised above its boiling point. The close relation between boiling temperature and pressure may be shown by the experiment illustrated in Fig. 32. In a round-bottomed glass flask water is boiled for some time, and when the steam has been coming off sufficiently long to have driven out all of the air, the heat is withdrawn and the flask closed by a tight-fitting cork. It is then inverted and clamped, as shown in the figure. If the bottom is then cooled by wringing out cold water from a sponge, the water begins to boil again. The explanation is as follows. When the flask was closed and inverted, the space above the water was filled, not with air, but with vapor of water. When the upper part of the flask was cooled by the application of cold water from without, its first effect was to condense a portion of this steam. Hence the pressure upon the surface of the water was much reduced, and the water started to boil because the tension of the vapor at its surface was greater than the pressure for the time being. As soon as boiling liberates more steam the pressure becomes greater again and boiling ceases.

FIG. 32.



Boiling under reduced pressure.

An important application of the fact that water and other liquids evaporate more rapidly under reduced pressure is found

in the use of vacuum-pans and apparatus for concentration of liquids *in vacuo*.

Under a pressure of 2 atmospheres ($14.7 \times 2 = 29.4$ pounds per square inch), water boils at 120.6° C., and under 10 atmospheres at 180.3° C. Based on this principle is the *digester*, a cylindrical cast-iron vessel which is used in chemical operations in which a substance is to be extracted, or two or more compounds react on one another under high pressure and temperature. By means of a vacuum-pump water may be made to boil at any temperature from 100° C. down: in an absolute vacuum it would boil at 0° C. Since the boiling point of fluids depends on the atmospheric pressure, and as we ascend from the earth's surface this diminishes to the extent of 1° C. for each 1080 feet, by ascertaining the boiling point of water, the height of mountains may be determined. On the summit of Mont Blanc water boils at 85° C.

2. *For a given pressure, every liquid has a definite constant boiling point.* This law is analogous to that governing the fusing point of solids. As a consequence of this law we are able not only to identify, but to separate various fluids from one another by means of their boiling points.

3. *Whatever be the intensity of the source of heat, as soon as ebullition begins the temperature of the liquid remains stationary.* On introducing a thermometer into the vapors* of a boiling fluid, the mercury will rise until it assumes the temperature of the surrounding vapors; it will then remain constant until the entire fluid has been vaporized. Should there be a mixture of miscible liquids, as water and alcohol, the boiling point will cover several intermediate degrees between those of its constituents. If the fluids are immiscible, the boiling point of the mixture will be lower than either of its constituents. Advantage is taken of this fact in removing the essential oils (which have high boiling points) from plants by distillation with steam.

Additional Causes accelerating Evaporation.—The rate of evaporation depends (1) on *temperature*, for increase of temperature accelerates evaporation by increasing the elastic force of the vapors. (2) *Increased surface:* the larger the area of surface the greater the number of exposed points from which

* The temperature of the boiling fluid may vary according to the nature of the vessel and the presence of dissolved matter, while that of the vapors remains constant.

vapors may be formed. For this reason fluids are stirred constantly or exposed in thin layers while evaporating. (3) *Removal of moist air* from the surface of a liquid facilitates evaporation, because vaporization cannot take place in an atmosphere already saturated with the vapor of the same fluid; hence the moisture-laden atmosphere should continually be removed and replaced by fresh dry air by fanning.

Influence of Dissolved Substances on Boiling Point.—The presence of dissolved saline matter raises the boiling point of a solvent, and as the proportion of this increases the rate of vaporization is retarded accordingly. Water saturated with common salt boils at 102° C., with calcium chloride at 179° C. During evaporation, as the solution becomes more concentrated, a saline pellicle forms upon the surface which effectually prevents any further evaporation unless continually broken by stirring.

Nature of the Vessel.—While the temperature of boiling water, when heated in a good heat conductor, as a metallic vessel, is 100° C., it will rise as high as 105° C. in vessels of such poor conductive material as glass or porcelain. The temperature of the fluid in the latter may be lowered to 100° C. by placing a piece of metal in the bottom of the vessel.

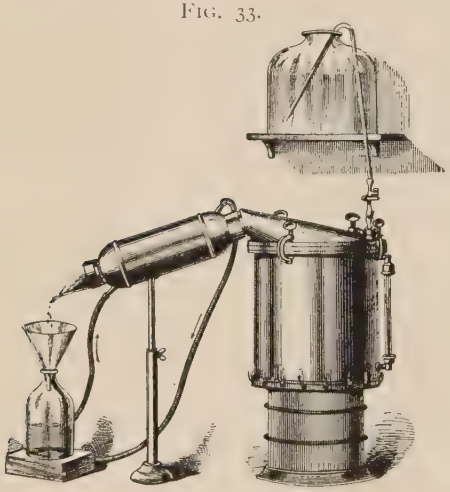
Production of Cold by Vaporization.—If a volatile liquid like alcohol or ether be poured on the hand, a cooling sensation is produced; the more rapid the vaporization and the more volatile the liquid the greater the intensity of cold. The explanation of this is that when a change of a solid into a liquid, or a liquid into a vapor, takes place, an absorption of heat follows: thus, when ether evaporates, the heat necessary for vaporization is absorbed from the surrounding objects, thereby producing cold. The heat absorbed in vaporization is far in excess of that required for liquefaction: thus, 1 gramme of ice requires only 80 calories to melt it, while 1 gramme of water requires 537 calories for vaporization; or, stated in other terms, the *latent heat of the liquefaction* of ice is 80 heat units, while the *latent heat of the vaporization* of water is 537 heat units. The most effective forms of refrigerating apparatus are based on this fact; in these, the rapid volatilization of such liquefied gases as ammonia or sulphur dioxide is facilitated by aid of condensing pumps. Solutions of brine cooled by contact with these rapidly vaporizing liquids may be carried for distances through coils and utilized for cold storage. Beginning with an easily liquefiable gas, and utilizing the low temperature produced by its vaporization under

reduced pressure* and the application of pressure, other more refractory gases are liquefied, and these in turn are employed for the liquefaction of still others: thus, step by step, physicists have succeeded in liquefying every known gas.

Condensation of Vapors.—This is the reverse of evaporation. It takes place whenever the temperature of the vapor drops below the boiling point of the liquid. It may, however, be also effected by pressure or because of the chemical affinity of the vapors for some other substance. By combining the influences of cooling and pressure, the most volatile of vapors have been condensed.

Distillation is an operation by which, taking advantage of the volatility of a liquid, we may separate it from dissolved or admixed solids or other liquids of higher boiling point. The fluid to be distilled is placed in the body of a *still*, which consists of copper,—plain or tinned inside,—or of glass if it be a retort; upon heating, the vapors of the boiling liquid rise and pass over and are condensed in the *condenser*, which may consist either of a plain straight tube of glass enclosed in a larger one, between which cold water circulates (this form is known as the Liebig condenser), or a worm, which is a long tube of block tin bent in the form of a coil and placed in a vessel of cold water. The form of condenser shown in the illustration (Fig. 33) consists of a series of short tubes

FIG. 33.



Remington still.

* BOILING POINTS OF LIQUEFIED GASES (760 MILLIMETERS).

Sulphur Dioxide	—10° C.	Nitric Oxide	—154° C.
Chlorine	—33° C.	Oxygen	—183° C.
Ammonia	—38° C.	Argon	—185° C.
Carbon Dioxide	—78° C.	Air	—192° C.
Nitrous Oxide	—88° C.	Nitrogen	—195° C.
Ethylene	—102° C.	Hydrogen	—243.5° C.

which afford as much condensing surface as a single long tube.

In this way water may be separated from the impurities, both gaseous and solid, which it contains, and the product is known as "distilled water," the purest form for chemical and pharmaceutical purposes. Alcohol or ether may be recovered from various solutions after they have been used as solvents to extract some valuable constituent from a crude drug. In manufacturing operations the same principle is utilized on an immense scale, as in petroleum refining, where fractional distillation is the means adopted to separate the various components of the mixture known as crude petroleum, and in the preparation of alcohol and alcoholic liquors from the products of fermentation.

IV. Transmission of Heat.

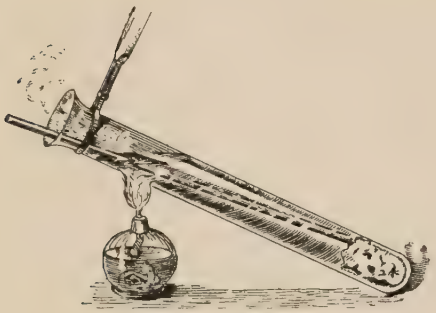
Both the heat and the light vibrations travel through ether from the source of heat or light without raising the temperature of the intervening space. When they strike upon a body to which these vibrations can be communicated, it feels the effects of heat and the temperature is raised. Such heat is called *radiant* heat, and it is said to be radiated from the source of heat.

If, however, the end of a metal bar is heated, a rise of temperature is soon recognized some distance from the heated spot, and it may extend throughout the entire length of the bar. The heat is here transmitted through the particles of the metal, and the molecular vibration is not merely an instantaneous one passed on, as in the case of heat rays radiating through air or ether, but continues for some time, and shows its effect in the rise of temperature. The heat in this case is propagated by *conduction.*

1. Conduction of Heat.—We find great differences in the ease with which bodies conduct heat. We have good conductors and bad conductors. Among solids, metals are the best conductors, while glass, resins, and wood are poor conductors. Liquids and gases are also poor conductors of heat. Both vegetable and animal tissues are poor conductors of heat. Cotton, wool, straw, and bran are all bad conductors. The relatively poor conducting power of liquids is shown in the experiment illustrated in Fig. 34. Snow may be packed in a test-tube and water put above it. On inclining the tube as shown in the cut, and applying the heat at the top of the liquid, the water may be made to boil without melting the snow. Poor conductors of heat are used both for

the purpose of retaining heat and shutting it out from bodies or spaces to be kept cool. Thus, steam-pipes at all times and water-pipes in winter are packed in asbestos, magnesium carbonate, straw, felt, and other non-conducting materials, to prevent the loss of heat. Ice, on the other hand, is packed in sawdust or shavings to keep out the heat and prevent its rapid melting. Fire-proof safes have the spaces between the inner and outer plates packed with non-conducting material, so that, while the outer frame may be heated red-hot, the inner frame does not become heated sufficiently to injure the books and papers that the safe may contain. Snow is a bad conductor of heat, and a layer of snow is capable of keeping the earth under it warm.

FIG. 34.



Water a non-conductor.

2. Radiation of Heat.—That the heat rays emanating from a source of heat are propagated through space without heating it is shown when a screen is interposed in the path of the rays. The sensation of heat at once disappears, as the surrounding air has not been heated to any notable degree by the heat rays passing through it. That radiant heat is propagated in vacuo can also be shown by experiment, and is in accordance with probability, as the radiant heat of the sun comes to us through space outside of the earth's atmosphere.

Of the laws governing the intensity of radiant heat we need only note the one that the intensity is inversely as the square of the distance. We will see later that this accords exactly with the observation of the nature of the light rays, and shows the close relationship between them. Radiant heat, when it strikes upon a body, may be reflected, diffused, absorbed, or transmitted. From polished surfaces, whether plane or curved, the heat rays are reflected or thrown back. But this reflection is never complete. Some of the rays are irregularly reflected or diffused. On the other hand, bodies which are poor reflectors absorb the heat rays in large amount. Such bodies, like lampblack, white

lead, and other finely divided substances, absorb the bulk of the rays which strike upon them. Among transparent substances, a notable difference exists in the readiness with which they transmit the heat rays. Rock-salt in transparent plates transmits the heat rays very perfectly ; alum, on the other hand, absorbs the rays and transmits very little.

3. **Convection.**—Liquids, as before stated and illustrated, are poor conductors of heat. When heat is applied to a liquid like water, the conductivity is so slight that, as shown in Fig. 34, ice or snow contained in the same vessel will not be melted, although the water may be brought to boiling at the top of the vessel. It is different, however, when heat is applied at the bottom of a vessel containing water or other liquid. The layer of the liquid nearest the point where the heat is applied becomes heated and at once moves upward, while a current of colder liquid moves downward to take its place. It is by these currents, which move the particles of the liquid from one place to another continuously, that the heat is mainly distributed, and not by the conductivity of the liquid. These ascending and descending currents may be made visible by putting a little bran or sawdust into the water before applying the heat. This mode of transmitting heat is called *convection*. Heat is also propagated in gases in the same way, as their conductivity is equally slight.

V. Apparatus Based on the Application of Heat.

Steam Engines.—Heat energy, generated in various ways, has been extensively utilized for labor-saving purposes. Machines in which heat generated by combustion is changed into mechanical energy, chiefly by the intervention of steam, have long been in use, and to this change of energy are now to be added the additional ones of the generation of light and electrical energy from the mechanical power developed by heat.

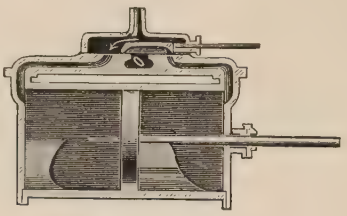
Engines in which heat is transformed into mechanical energy include hot-air engines, steam engines of various kinds, and engines driven by exploding gas or mixtures of gas and air.

In the steam engine the power is obtained from a piston moving in a cylinder (Fig. 35) while steam is alternately admitted to either end of the cylinder, and so moves the piston back and forth.

Steam engines may be divided into the two classes, non-condensing and condensing engines, according as they exhaust their steam from the cylinder directly into the air or have it condensed

by the admission of a spray of water into the exhaust end of the cylinder. The latter are the more effective, as the back press-

FIG. 35.



Steam cylinder.

ure in the cylinder is reduced to a fraction of an atmosphere instead of being the full atmospheric pressure, as in the non-condensing engine.

Engines are termed, according to the use to which they are to be applied, stationary and locomotive engines.

In hot-air engines the elastic force of hot air is made to drive the piston, and in gas engines the expansion of a mixture of gas and air at the moment of explosion.

The vapor of light petroleum naphtha is also used as a source of power in the naphtha motors and engines. A portion of the naphtha in burning generates the heat, and a second portion is vaporized in a highly heated chamber, and by its explosion drives the piston.

CHAPTER V.

RADIANT ENERGY.—II. Light.

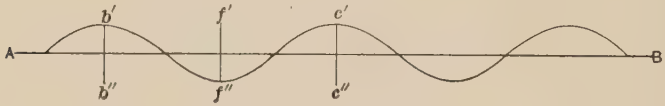
I. Nature of Light.

1. Comparison of Heat and Light.—We have already spoken of the undulations or vibrations which, radiating out from sources of light like the sun, are communicated to the ether, an exceedingly attenuated elastic medium which fills space, and are thus propagated until they strike upon bodies whose molecules are capable of taking up the vibrations and developing what we call heat energy. We saw also that chemical combination or combustion, friction, and other causes were capable of initiating these vibrations and serving as sources of heat. The sun, the great source of these heat vibrations, and most other sources of heat, are also capable of radiating undulations of a more systematic, wave-like character, which have one or both of two different effects. They may act upon the retina of the eye, and when communicated by the optic nerve may produce upon the brain the sensation of vision, or they may act upon certain chemical salts, decomposing them, because of what is called actinic power. Most generally, sources of heat become sources of light when the molecular vibration becomes more rapid, as the light undulations are more rapid and of shorter wave-length than the heat rays. Thus, a bar of metal, when heated, gives off at first only heat vibrations recognizable by the rise in temperature. After a time a red glow begins to appear and light rays of greatest length and slowest time of vibration are emitted. When the iron is still further heated it becomes white-hot, and the waves are now of shortest wave-length and quickest vibration. The wave-motion communicated by heat and light to ether consists of vibrations which are perpendicular to the line of propagation. As shown in Fig. 36, the wave line represents the motion of the ether molecules in the direction A B, the distance $b'\ c'$, from one wave-crest to the next, is a *wave-length*, while the distances $b'\ b''$, $f'\ f''$, $c'\ c''$ represent the *amplitudes* of vibration.

Theory assigns no limit to the length of ether waves, for the

optic nerve is sensitive to only a limited number, the shortest being 0.000039 centimeter long, corresponding to 757 million million vibration-frequencies per second, while the longest is 0.000076 centimeter, with 392 million million vibrations. All

FIG. 36.



Wave-motion.

vibration-frequencies which lie between these limits constitute light. Each wave-length with its vibration-frequency represents a particular kind of light, which produces the sensation of color.* Color is then simply the impression resulting from some particular wave-frequency. Waves of minimum vibration-frequency produce the sensation of red, while those of maximum frequency that of violet; those lying between these produce sensations of red, orange, yellow, green, and blue. Such a succession of colors, beginning with red and shading gradually from one to the other and finally to blue, is called a *spectrum*. Those colors at the red end of the spectrum (ultra-red to yellow) are the richest in heat and poorest in actinic rays, those at the violet end (blue to ultra-violet) give no heat, but are very active chemically (actinic) (see p. 168), and those nearest yellow give the most light. Ordinary white light consists of these various long and short waves.

A *luminous* body is one which emits light rays. Bodies may be self-luminous or original sources of light, like the sun, a candle-flame or gas-jet, and a fire-fly, or merely illuminated bodies which shine by reflected light, like the moon and bodies lighted by ordinary daylight.

Luminescence.—Certain fluids and solids, when placed in

* LIGHT WAVES.

Color.	Vibration-frequency.	Wave-length.
Ultra-red	370 million million	.0000810
Red	428 " "	.0000700
Orange	502 " "	.0000597
Yellow	516 " "	.0000580
Green	569 " "	.0000527
Blue	634 " "	.0000473
Violet	739 " "	.0000406
Ultra-violet	833 " "	.0000360

radiations of wave-frequency which are too great to excite vision, emit a peculiar light,—that is, these bodies render visible otherwise invisible radiation. Luminescence may be of two kinds, according to the degree of duration,—namely, *fluorescence* and *phosphorescence*. Fluorescence is limited in duration, lasting as long as the substance is exposed to the proper light radiation. Solutions of quinine sulphate, gelsemic acid, eosin, fluorescein, chlorophyll, etc., belong to this class, and emit different colors according as they are viewed by either transmitted or reflected light. Thus, an ethereal solution of chlorophyll is green and an aqueous solution of eosin is red by transmitted light, while by reflected light the former is red and the latter is yellow. Phosphorescent bodies are those which, after exposure to the light, continue to shine for some time in the dark. As examples we may cite the glowing of phosphorus and the fire-fly ; and some chemicals, as calcium and strontium sulphides, when exposed to sunlight, also become phosphorescent in the dark ; this lasts sometimes for thirty hours.

Transparent bodies are those which readily transmit the luminous rays. *Translucent* bodies transmit light less readily, so that at most the outlines of bodies can be seen through them. *Opaque* bodies do not transmit light at all, and cut off the light rays completely. Some bodies, like metals, which are opaque in bulk, become translucent or even transparent when in very thin layers. A *shadow* is the space where the light rays have been intercepted by an opaque body lying in their path.

2. Transmission, Velocity, and Intensity of Light.—In a homogeneous medium the light rays are always propagated in a straight line. This is illustrated when a beam of sunlight enters a dark room. Its path is revealed by illuminated particles of dust and shown to be in a straight line.

Light travels through space with great velocity. Accurate observations made by astronomers have allowed this velocity to be calculated with considerable exactness. It has been found to be about 186,000 miles in a second. Determinations by physical methods have confirmed these figures.

The intensity of illumination on a given surface is inversely as the square of its distance from the source of light. That is, a given unit of surface at twice the distance from the source of light of another surface will receive one-fourth the light.

Photometers are instruments for measuring the relative intensities of light. The form in common use is the Bunsen or bar

photometer. It consists of a screen of paper mounted in a box which slides to and fro on a graduated bar. The paper screen has a central spot saturated with paraffine. Fixed at one end of the bar is a standard light, usually a sperm candle, of definite weight, while the light to be compared is placed at the other end of the bar. If the two lights are of equal intensity, the grease-spot does not show on the paper. When one side is more strongly illuminated the spot appears dark on that side and light on the other. It is then necessary to move the box containing the paper screen until the spot just becomes invisible. Its position on the bar is then noted, and the relative distance from the two ends taken for the calculation. The result is usually referred to a standard candle and expressed in what is called candle-power.*

II. Reflection of Light.

We have before spoken of the path of a ray of light entering a dark room, as shown by the illuminated particles of dust, to be a straight line. If this ray strike obliquely upon a horizontally placed mirror or polished surface, we will also notice that a ray of light is thrown off or *reflected* from the mirror, and on measuring the angle made by the entering ray and the horizontal mirror, and that made by the reflected ray and the mirror, they will be found to be equal (Fig. 37). From the experiment we may deduce the following two laws of the reflection of light : †

1. The angle of reflection is equal to the angle of incidence.

2. The incident and the reflected ray are both in the same plane, which is perpendicular to the reflecting surface.

Not all of the light of the incident ray or beam is, however, reflected in this way. Unless the reflecting surface be an absolutely smooth one, some of the light is irregularly reflected or

---

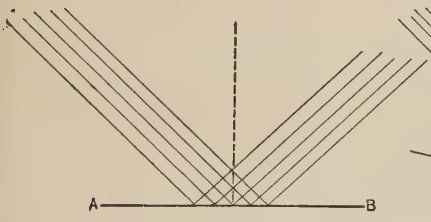
* The standard of comparison is a sperm candle burning 120 grains per hour. If the distance from the illuminated spot to the standard candle be 2 feet, and to the light to be compared 6 feet, the candle-power of the light would be 9. For, according to the law the *intensity of illumination from a luminous point is inversely proportional to the square of the distance of the illuminated surface from that point*, then $\frac{6^2}{2^2} = \frac{36}{4} = 9$. The following table gives the relative brightness of several sources of light.

Standard candle	1 candle-power.
Gas-jet	12 to 18 " "
Welsbach burner	30 to 50 " "
Electric arc	800 " "

† Compare with p. 26.

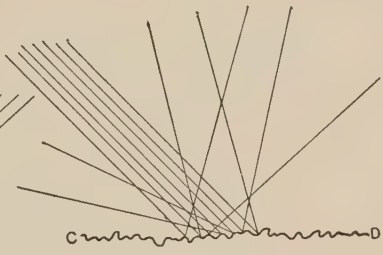
diffused. It is this which enables us to see objects. Well-polished surfaces like that of a mirror reflect light in a definite direction (A, B, Fig. 37), while rough or dull surfaces scatter

FIG. 37.



Reflection of light.

FIG. 38.



Diffusion of light.

or diffuse the light : C, D, Fig. 38, represents the roughness of the surface of paper very much exaggerated. This diffused light renders it visible in all directions. If a reflecting surface were absolutely smooth, it would be invisible. We would simply see in it the image of other objects. Objects about us are thus illuminated by the diffused light reflected from the clouds, the air, and other surfaces, and so they become visible, although they may not receive the direct rays of light from the sun. There are in fact many days when, on account of clouds, our illumination comes wholly from this irregularly reflected or diffused light.

Reflection of Light from Polished Surfaces.—*Mirrors* are bodies with polished surfaces which are employed to show by reflection objects placed before them. *Images* of the objects are thus formed. The development of these in the case of plane mirrors is very simple. The rays of light coming from the object before the mirror make with the latter an angle of reflection equal to the angle of incidence, and so come to the eye. But the eye always sees objects in the direction from which the rays reach it, so that the image appears in the prolongation of the reflected ray, and at a distance back of the mirror exactly equal to that of the object from it in the other direction. The image, therefore, is not a *real* one formed by the reflected rays themselves, but an apparent or *virtual* image only. It is also a reversed image as regards right and left, as is shown when printed matter is held before a mirror. Wood-cuts and type must therefore be made in reversed position. When these are held before

a mirror the image shows as a printed impression from the type will appear.

The ordinary glass mirror has in reality two reflecting surfaces, that of the glass and that of the metallic backing of the glass. Ordinarily we see only the one image, because the metallic backing is a much better reflector than the glass surface, but we can readily get the double image by placing the point of a pencil against the glass surface, when the double image allows us to judge of the thickness of the glass.

Transparent bodies the surface of which is smooth may reflect light quite regularly at times, and so form distinct images. An illustration of this is seen in the reflection of foliage and other objects in the still waters of a clear stream or pond.

All the images thus far spoken of have been formed with plane mirrors, and have been virtual images. With concave mirrors of glass or polished metal the reflected rays themselves may be made to unite to form an image, which is therefore a real image and is seen on the same side of the mirror as the object itself. This image, formed by the reflection of the rays themselves, will, however, be inverted, because the rays from different parts of the object after reflection must assume relatively reversed positions with reference to each other. The *focus* of a spherical concave mirror is a point to which the reflected rays tend to converge. If the incident rays are parallel to the axis of the spherical mirror, the focus is called the principal focus. When the object is farther from the mirror than the principal focus, the image will be inverted and real, as well as smaller than the object; when the object is between the principal focus and the mirror, the image is virtual and erect, as well as larger than the object.

With convex mirrors we have virtual images only, appearing behind the mirror, erect and smaller than the object.

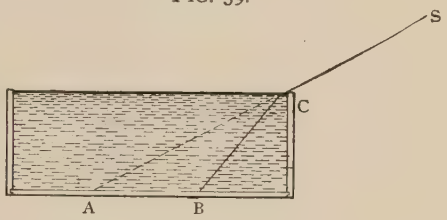
III. Refraction of Light.

1. Theory of Refraction.—When light passes obliquely from one transparent medium into another of different density, as from air to water, it is bent from its course, or *refracted*. The rule for this refraction is simply stated. When light passes from one medium into a denser medium, it is bent toward a perpendicular line; when it passes into a rarer medium it is bent away from the perpendicular line.

The phenomena of refraction may be illustrated in the experiment shown in Fig. 39. A water-tight rectangular box is con-

structed, of which one side is a plate of glass. Place this in a dark room and allow a slender beam of light, S, to enter in such direction that it will just pass over the edge of the box at C, making the line A, C, S. Fill the box with water and make this slightly cloudy with a few drops of an alcoholic solution of mastic or sandarac. The beam of light will now be bent at the surface of the water, and will take the direction B, C, S. As it passes from the lighter medium air into the denser medium water, it is bent toward a line perpendicular to the surface.

FIG. 39.



Refraction of light.

Numerous familiar illustrations of the phenomena of refraction may be cited. If we place a coin in the bottom of a basin in such position that it is just hidden by the edge of the basin from the observer looking obliquely from the side, and then pour water into the basin, the coin becomes visible. The reflected rays of light on emerging from the water into air are bent away from the perpendicular, and as the eye sees the object in the prolongation of the ray which reaches it, we seem to see the coin at a point on the bottom beyond its true position. If one stand in a pool of clear water, the depth of which is everywhere the same, the bottom will appear to curve upward on all sides and the water deepest just below the eye of the observer. A few feet distant, water four or five feet deep may seem not over a foot in depth. If, however, the bottom seems flat, the water would grow deeper as one walked outward from the point of observation. The danger of such a deceptive appearance is obvious.

The angle made by the incident ray of light with the perpendicular is called the *angle of incidence;* that made by the refracted ray with the perpendicular is called the *angle of refraction.* The ratio between the lines of these two angles is called the index of refraction, and varies, of course, with the media.

When light passes from a denser into a rarer medium the angle of refraction is greater than the angle of incidence. When, in such a case, the angle of refraction becomes 90°, the angle of incidence is called the *critical angle,* because when the angle of refrac-

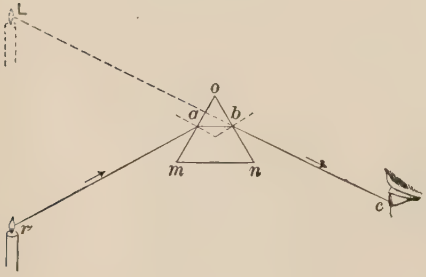
tion becomes greater than 90° the refracted ray will not emerge, but will be reflected back again from the surface of the denser medium. This is called *total reflection*, and is more complete than the ordinary reflection of light, where, because of the imperfection of the reflecting surface, some light is always irregularly reflected or diffused. The phenomena of total reflection can be easily shown by means of a glass cube, such as is often used for a paper-weight or inkstand. Objects below the cube are invisible through the side faces, because of this total reflection. Similar effects of total reflection of the images of objects contained in aquaria are frequently observed, and add greatly to the interest of their appearance.

The mirage seen in the desert and at times at sea is an optical illusion, by which inverted images of distant objects are seen as if below the ground or in the atmosphere, and is based upon the fact of total reflection, owing to the unequal density of the several layers of the atmosphere through which the rays of light pass.

2. Prisms and Lenses.—A prism is any transparent refracting medium bounded by planes inclined to each other. The angle made by the two sides through which the light enters and emerges is called the angle of refraction of the prism. Both flint and crown glass are in use as materials for prisms, but the former possesses the higher refracting power. We may note two effects of prisms upon light passing through them,—

1. Light of any kind is refracted or bent out of its course. A ray of light (*r a*, Fig. 40) falling on the prism, *o m n*, is refracted towards the perpendicular and passes through in the direction *a b*; here, in passing from a denser into a rarer medium, it is refracted from the perpendicular in the direction *b c*. The eye at *c* sees the object *r* backward along the ray *c b*, so that it appears at L.

FIG. 40.



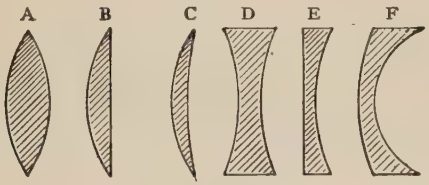
Refraction through prism.

2. White light is dispersed into a band or spectrum of colors. This second effect will be noted on p. 93.

Lenses are transparent media, usually of glass, which from the

curvature of their surfaces have the power of causing luminous rays either to converge or diverge. The combination of spherical surfaces, either with each other or with plane surfaces, gives rise to six kinds of lenses, which are illustrated in Fig. 41. A is a

FIG. 41.



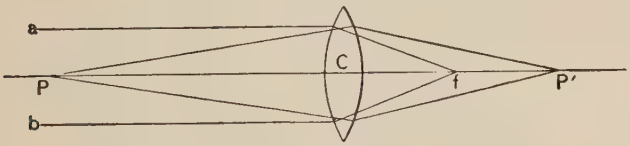
Lenses.

double convex, B a *plano-convex*, C a *concavo-convex* or *converging meniscus*, D a *double concave*, E a *plano-concave*, and F a *convexo-concave* or *diverging meniscus*.

The first three, which are thicker in the centre than on the edges, are converging in their effect on rays of light ; the others, which are thinner in the centre, are diverging.

A line drawn through the centre of a lens, as P P′, Fig. 42, is called its *axis :* a double convex lens will bring parallel rays of light *a* and *b* to a point along this axis which is called the *principal focus f*. The distance from the middle of the lens C to the principal focus *f* is called its *focal length*. This may be ascertained by focussing the rays of sunlight on a piece of

FIG. 42.



Principal and conjugate foci.

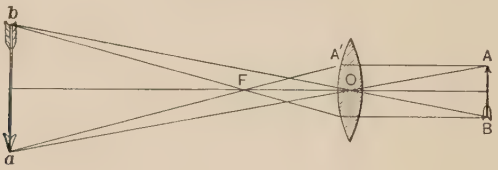
paper. Now, if a candle be placed at P, its rays diverge to the lens C, and will be brought to a focus at P′, beyond the principal focus ; if the light is placed at P′, the rays focus at P : these two exchangeable foci are called *conjugate foci*. Again, if the source of light be placed at the principal focus of the lens *f*, the refracted rays *a* and *b* will be *parallel ;* if the source of light be inside the principal focus, the refracted rays will *diverge*.

Images produced by Convex and Concave Lenses.—According

as the object observed is placed beyond or within the principal focal distance of a convex lens, we observe the following :

1. *A large object at some distance from a convex lens produces a small real inverted image a little beyond the principal focus of the lens.* Thus, in Fig. 43, *a b* represents the object and A B

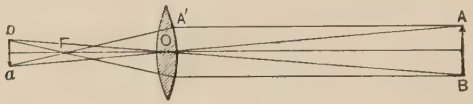
FIG. 43.



Double convex lens images.

the image. The rays cross one another in passing through the lens ; hence the image is inverted. An example of this is the photographic camera. Fig. 44 illustrates the magnification that

FIG. 44.

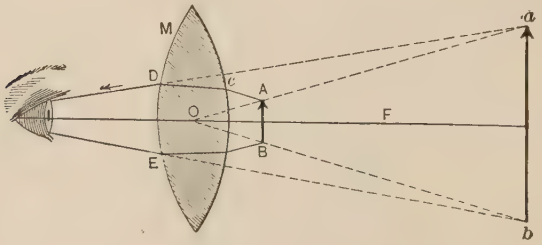


Double convex lens images.

takes place in the object-glass of a telescope, the object *a b* being at a very great distance beyond the focal distance of the lens.

2. *If an object be placed between a convex lens and its principal focus, an enlarged upright virtual image is produced, and*

FIG. 45.



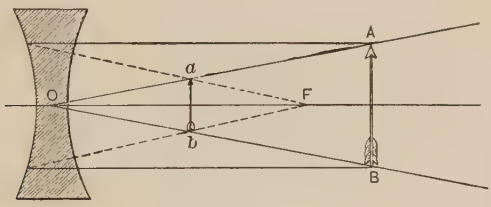
Simple microscope.

is apparently seen at a greater distance from the lens than the object. Thus, A B, Fig. 45, represents the object placed within

the principal focus F ; the eye observes the image A B, at *a b*, through prolongation of the emergent rays A D and B E to D *a* and E *b*. Such a double convex lens of short focus is called a simple microscope.

3. *Concave lenses produce virtual erect images smaller than the object.* Thus, A B, Fig. 46, is the object, and the rays

FIG. 46.



Double concave lens image.

coming from A are deviated so as to appear to come from *a*, situated on a line drawn from A to the optical centre O ; likewise, rays from B appear to come from *b*, on the line B O ; hence *a b* is the image of the object A B.

3. Decomposition of White Light—Spectrum.—We have already referred to the fact that the effect of a prism upon a beam of light passing through it is twofold,—that, in addition to the refraction or bending from its course, white light is decomposed into a series of colored rays. The explanation of this is, that the rays which make up solar and other varieties of white light are not equally refrangible, and hence in passing through a prism they are dispersed and form a band of colors known as a *spectrum*. This is illustrated in Fig. 47.

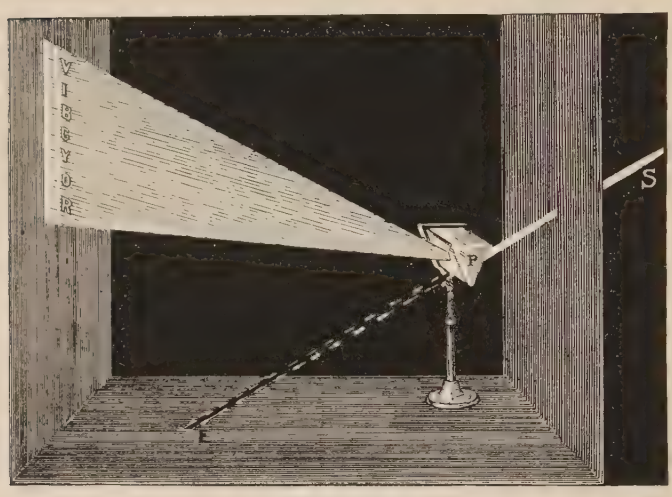
If a beam of white light, S, be allowed to strike upon a prism, P, it is all refracted, but the component parts are refracted in different degrees, the red rays least, the orange next, and then the yellow, green, blue, indigo, and violet in the order named. The result is that, instead of a spot of white light appearing on the floor, E, a band of seven colors appears upon the wall or a screen placed at a height above the floor. This band is, in reality, a series of overlapping images of the sun, which can be again superposed by means of a double convex lens, when there will appear in the focus of the lens a white spot.

While the colors of the solar spectrum merge imperceptibly into one another, so that many tints might be said to exist, the colors cannot be decomposed further, as when the red rays or any

of the others taken singly are passed through a second prism they are uniformly refracted and give a spot of red or other color. These colors are, therefore, homogeneous, and light composed of them is known as *monochromatic* light.

The seven colors of the spectrum may be reunited to form white light in a variety of ways. If the spectrum formed by one

FIG. 47.



Solar spectrum.

prism be allowed to fall upon a second prism of the same material and the same refracting angle as the first, but inverted, the latter reunites the several colors and the emergent pencil is colorless. A concave mirror upon which the spectrum may be cast will also reunite the colors, and a white spot will be formed in the focus of the mirror.

The recomposition of white light from the colors of the spectrum may be shown most strikingly by the aid of Newton's disk. This is a card-board disk about a foot in diameter, on which are pasted alternate segments of colored paper in the order of the colors of the spectrum. When this is rotated rapidly, the eye receives the impression of white light. This is due to the fact that sensation is of longer duration than the impression from which it results. If a new impression acts before the sensation arising from the former one has ceased, a sensation results which consists of two impressions. If the time is sufficiently short,

several impressions may be mixed with one another. This also explains the phenomenon of the moving lantern pictures, as shown in the cinematograph, bioscope, etc.

Complementary Colors.—While the combination of all the colors of the Newton's disk produces white light, we may by the combination of individual colors get numerous composite shades. Thus, if we remove the red from the set of colors, on combining the remaining colors we get a bluish-green. This is then said to be the complementary color to red, because when united with it white is produced. Similarly, purple is the complementary color to green, and an ultramarine blue to the yellow.

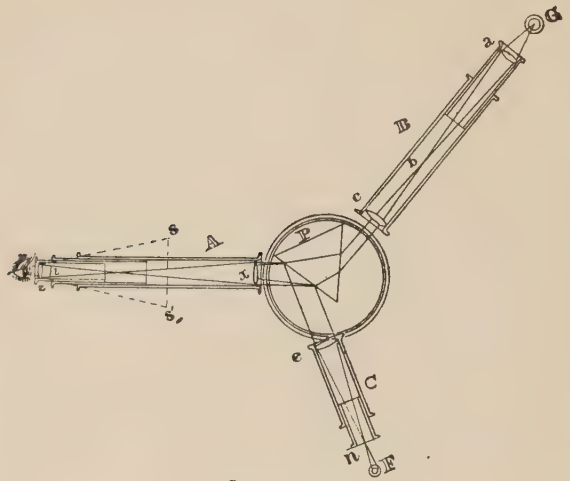
It must not be understood that two pigments showing such colors complementary to each other when mixed yield a white product, but that the two color impressions when superposed give the effect of white light. Thus, if chrome-yellow and ultramarine blue be mixed, the result will be a green pigment, while a yellow and a blue light combine to give us white as the resultant.

The color of bodies depends upon the manner in which they act upon white light. A portion of the rays is absorbed, and that which remains determines the color of the body. If the unabsorbed rays traverse the body, it is colored and transparent; if, on the contrary, they are reflected, the body is colored and opaque. In both cases the kind of light rays (wave-frequencies) that are not absorbed gives the color. If a body absorbs all the colors, it is black; if it reflects or transmits all, it is white or colorless. A body appears blue when it absorbs all the colors except blue.

4. Spectrum Analysis—Spectroscope.—The examination of the light from different luminous bodies by the aid of a prism has led to important discoveries as to the nature of the light and the luminous bodies. This study has been made possible by the aid of the spectroscope first proposed by Bunsen and Kirchhoff. A sectional view of this instrument is given in Fig. 48. The rays from the source of light, G, falling upon the lens a, are made to converge at b, the principal focus of the lens c, so that they are thrown as parallel rays upon the prism P. After refraction, they fall upon the lens x, which forms a real and reversed image of the spectrum at i. This is magnified by the eye-piece so that a virtual image is formed at ss' much enlarged. The third arm of the instrument, C, is for the purpose of throwing upon the prism, and so into the observing telescope, an image of a micrometer scale which has been photographed upon

glass at *n*. By its means the relative position of lines or bands seen in the spectrum can be determined.

FIG. 48.



Spectroscope.

When examined by the aid of such a spectroscope, we find that luminous bodies are capable of yielding three different kinds of spectra.

If the light from a white-hot solid or liquid body be examined, a continuous band of all the colors from red to violet will be observed. Such a spectrum is called a *continuous spectrum*. When the glowing body is in the condition of gas or vapor, we have a series of bright lines or bands against a black background. This is termed a *bright-line spectrum*. When, however, sunlight is examined by the spectroscope, the continuous spectrum appears crossed by hundreds of dark lines. The light from the fixed stars is similar, and such spectra are called *absorption spectra*. The dark lines of the solar spectrum, known as Fraunhofer's lines, were first fully explained by Bunsen and Kirchhoff, who proved that many of them corresponded to the bright lines obtained in the spectra of the vapors of such metals as sodium, calcium, iron, etc.

They therefore suggested the following explanation of the solar spectrum. The sun is probably an intensely glowing solid or liquid mass. This would give a continuous spectrum without either bright or dark lines. But the glowing mass is surrounded by an atmosphere containing cooler (although brillant) metallic

vapor. This vapor would absorb light of the same kind as it emits, and hence dark lines would show in the spectrum in the same position as those occupied by the ordinary bright lines of these metallic vapors. This theory has been rendered very probable by experiments in which the bright lines of elements like sodium have been reversed and caused to appear as dark lines by passing the light from a very hot sodium flame through a cooler flame of the same vapor. We can also increase the natural absorption by causing the sun's light to pass through more sodium vapor placed in front of the spectroscope slit.

The study of the spectra of various elements, and the accurate mapping of the dark lines of the solar spectrum, show that a large number of the metals known to us on the earth occur as vapors in the sun's atmosphere.

With the aid of this method of spectrum analysis chemists have discovered a number of new and relatively rare metals, such as cæsium, rubidium, thallium, indium, gallium, and scandium. It has also furnished an invaluable means of detecting impurities in chemical preparations which would otherwise escape notice.

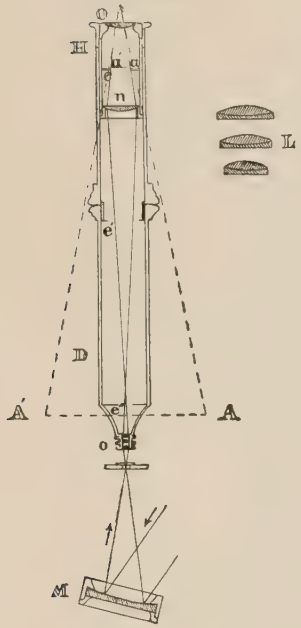
Absorption spectra of a somewhat different character are also obtained when solutions of coloring matters like chlorophyll, hæmateïn, etc., are placed in glass cells and interposed between a source of light and the slit of the spectroscope. Broad absorption bands show, extinguishing at times the whole violet end of the spectrum.

IV. Optical Instruments based upon the Use of Lenses.

1. The Microscope.—The simple microscope, as we have seen, is merely a double convex lens of short focus, by means of which we can look at objects placed between the lens and its principal focus. The image produced is an erect and magnified virtual image of the object. In the simple microscope the measure of the linear magnification produced is the ratio of the apparent diameter of the image to that of the object, while the superficial magnification is the square of this ratio. The compound microscope consists essentially of two condensing lenses: one with extremely short focus, called the object-glass or objective, because it comes down immediately over the object; the other acts simply as a means of magnifying the image formed by the first and is called the eye-piece. The method of combining these lenses and the formation of images by means of them is illustrated in Fig. 49. In this case the objective, *o*, consists of three

small condensing lenses, which together act like a single very powerful lens. The object is placed on the stage, and the rays, passing through an additional lens at *n*, inserted here to render the image achromatic, form a real and magnified image at *aa'*. This image is then magnified by the lens o and a much magnified virtual image is formed at AA'. The two lenses, *n* and o, together constitute in this case the eye-piece, just as the three small lenses, *o*, constitute the objective. The magnifying power of the compound microscope is obtained by multiplying the magnifying power of the objective by that of the eye-piece. Thus, if the magnifying power of the lens *o* is 50 diameters and that of the lens o is 4 diameters, the image seen will be magnified 200 diameters, or the superficial enlargement will be 40,000 times the natural size of the object. The degree of magnification is often determined experimentally by means of a micrometer eye-piece fitted to the microscope.

FIG. 49.



Compound microscope.

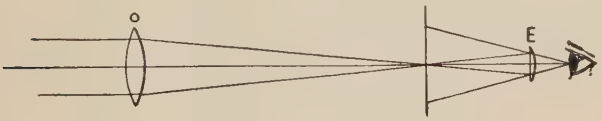
Spherical Aberration.—Thus far it has been assumed that all the rays of light in passing through a convex lens meet at the same focal point on the other side. This is correct for lenses whose aperture is not greater than 10°. When larger, it will be found that those rays which pass through the edges of the lens are refracted more than those passing through the centre. This results in scattering the rays from the focus, producing an indistinct image. This is called spherical aberration, and can be corrected by placing in front of the lens diaphragms provided with round apertures in the centre, called *stops*, which cut off the rays from the edges and allow only the passage of the central ones nearly parallel to the axis. A great sharpness of definition is gained, but brightness of illumination is thereby diminished. Such stops are seen in the caps covering the eye-piece of the microscope; also in the opera-glass and telescope. In the photographic lens the

stops are adjustable, owing to the necessity of employing apertures of different sizes.

Chromatic Aberration.—Since a lens is a combination of an infinite number of prisms, it not only refracts light, but also decomposes (disperses) it, like a prism, into different-colored rays of different degrees of refrangibility, which produce a confused coloration of the margins of the images. This scattering of the colored rays to different foci is called chromatic aberration. It may be corrected by employing an *achromatic combination*, in which two lenses of unequal dispersive power are fitted together, one being the double convex (converging) lens of crown glass, while the other is a concave (diverging) lens of flint glass. Such achromatic combinations are seen in L, Fig. 49, which are enlarged representations of the objectives, O.

2. **The Telescope** is a combination of two or more lenses to enable one to view distant objects,—that is, it increases the angle under which the object is seen. It consists of a large,

FIG. 50.



Astronomical telescope.

double-convex object lens, O, Fig. 50, which forms an inverted image of the distant object at its focus. This is in turn enlarged by the plano-convex lens, E, which serves as eye-piece. For astronomical purposes the object-glass is made as large as possible, in order to secure the greatest amount of light in observing faint, distant objects. The greater the diameter of the objective the longer is its focal length; thus, the Yerkes 40-inch objective has a focal length of about 64 feet. To find the magnifying power, divide the focal length of the object-glass by that of the eye-glass. The *terrestrial* telescope, or spy-glass, differs from the astronomical in having two additional condensing lenses, which restore the inverted image to the erect position. The *Galileo* telescope, now used in the form of the opera-glass, consists of a double convex lens, which collects the rays from an object, and a concave (divergent) eye-piece, which serves to make the convergent rays of the objective parallel, producing an erect, virtual, and magnified image.

3. **The Lantern and Camera.**—The projecting lantern, or

stereopticon, is used for throwing magnified images on a screen in a darkened room. It consists of a closed box of wood or metal in which is placed a strong oil lamp provided with a reflector or a lime light. In the front of the box are fixed one or two plano-convex lenses which converge the light upon the lantern-slide, which is a photograph, drawing, or painting upon glass. Beyond this a double convex focussing lens is placed so that the slide shall be a little beyond its principal focus. The lens will then produce a real, inverted, and enlarged image upon a screen placed at a suitable distance. To get the image in proper position the lantern-slide is, of course, put in an inverted position. The image on the screen will be the more magnified as the slide approaches the principal focus of the lens, which is, therefore, set so as to be moved to and fro.

In the photographic camera we have the reverse of the projecting lantern. It is a dark chamber with a convex lens in front and a screen at the back on which to form an image of objects in front of and outside of the camera. This image is real, inverted, and usually smaller than the object. It is visible to the operator back of the camera, as the screen is made of ground glass, which, when side light is shut out, is semi-transparent. In order to form a sharp image the lens is given a movement to and fro, and the screen at the rear of the camera box is also capable of a forward and backward movement by means of a rack and pinion. When a clearly defined image is obtained, a cap is put in front of the lens, the ground-glass screen is removed, and a plate-holder containing a sensitized glass plate is slipped into its place. This brings the photographic plate exactly in the position of the screen, and the image will be cast upon it. The slide in front of the plate-holder is then drawn out and the cap removed from the lens, when the reflected rays of light quickly act upon the sensitive surface.

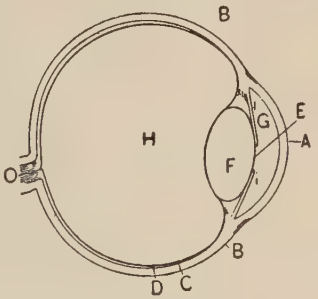
Photographic Processes.—The plates used at present in photographic processes are of two kinds: the "wet plates," with a film of collodion carrying the sensitive salt of silver, and the "dry plates," coated with an emulsion of gelatin and bromide or chloride of silver. To prepare the former, a glass plate is carefully cleaned and then a solution of collodion impregnated with iodide of ammonium or cadmium is poured upon it and allowed to flow to and fro until the plate is uniformly coated. The plate is then immersed for about a minute in a bath of nitrate of silver containing thirty grains of the salt to an ounce of water.

This latter operation, called the *sensitizing*, must be performed in a dark room. The plate is then allowed to drain and is placed in the frame for use in the camera. The dry plates are more generally used at present, because they are more sensitive than the others and can be prepared in quantity and kept, suitably preserved from light, for long periods of time.

On removing the plate from the plate-holder in the dark room after the exposure, no change is visible, but on pouring over it a *developing* solution, an image gradually appears, owing to a change in the physical condition of the silver salt, or a chemical reduction whereby some of the silver haloid is permanently decomposed. For developing, an alkaline solution of pyrogallic acid or a solution of ferrous sulphate and an oxalate are generally used, although many organic compounds, like hydroquinone and amido-phenol derivatives, which have reducing properties, are also found to act as developers. When the image has been sufficiently developed, the plate is washed and the unchanged iodide or bromide of silver is dissolved away by immersion in a bath of sodium thiosulphate (hyposulphite). The plate is then again washed, and the film containing the image, now known as a *negative*, is dried and coated with a thin coating of transparent varnish. From this negative may be printed *positives* on prepared or sensitized paper, or on glass suitable for lantern slides.

4. The Eye as an Optical Instrument.—The human eye is a camera, and the retina the sensitive surface upon which images are constantly formed to be communicated by the optic nerve to the brain.

FIG. 51.



Cross-section of eye.

The outer covering of the eyeball, the *sclerotic coating* (B, Fig. 51), or white of the eye, is quite firm and constitutes the frame of this camera. Inside of this is the *choroid coating*, C, which gives to the interior of the eye the black lining necessary for absorbing all useless or diffused rays. In front we have the transparent *cornea*, A, set in like a watch-crystal; the colorless and transparent *aqueous humor*, G, filling the space between the cornea and the *crystalline lens*, F; and back of this the jelly-like *vitreous humor*, H, filling the whole remaining cavity.

In front of the crystalline lens we have the *iris*, *i i*, a diaphragm with a circular opening which can be widened or contracted at will by muscular effort, the opening constituting the *pupil* of the eye ; and spread out over the rear of the cavity is the *retina*, D, which is the sensitive plate of the camera, and by its connection with the optic nerve conveys its impressions to the brain.

The eye, like the camera, requires to be focussed according to the varying distance of the object. This is effected mainly by a change in the curvature of the front of the lens. For instance, by a strong pressure of the ciliary muscles at either edge of the crystalline lens the curvature is increased, thus accommodating the eye for viewing near objects. When this muscular effort is relaxed, the lens again becomes flatter and is in adjustment for more distant objects. The eye is, therefore, rested by fixing it on objects at some distance. If the eye be now considered as an optical instrument, we will see that its crystalline lens, being a double convex lens, must form real and inverted images of objects placed before us. That the images formed on the retina of the eye are inverted, has been shown experimentally with the eyes of albinos, in which, on account of the absence of the choroid coating, the image is visible. That the brain is able to restore all these inverted images to the natural position without apparent effort is due mainly to training and the aid of the sense of touch, with which we have been accustomed to aid the vision from earliest infancy.

The distance of distinct vision varies greatly in different individuals. For small objects like print the normal distance is from ten to twelve inches.

Persons who see distinctly only at a short distance are called *near-sighted*, and those who see distinctly only at a long distance are called *long-sighted*. The usual cause of near-sightedness is a too great convexity of the cornea or the crystalline lens, in consequence of which the rays, instead of forming an image on the retina, are focussed at a point in front of it. The remedy is found in the use of diverging glasses, which tend to throw the focus farther back and so bring it upon the retina. The cause of long-sightedness is an insufficient convergency of the lens of the eye and consequent formation of images at a point back of the retina. With advancing age especially the crystalline tends to become flatter. The remedy is the use of converging glasses, which aid in bringing the rays to a focus exactly upon the retina.

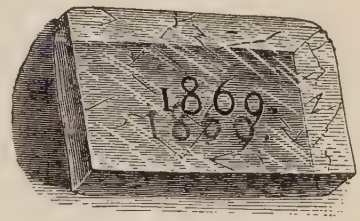
V. Double Refraction and Polarization.

1. Double Refraction.—Certain crystalline solids possess the property of dividing an incident ray which passes through them into *two* distinct rays, which undergo unequal refraction and produce two images. This phenomenon is known as double refraction, and is caused by inequalities in the grouping of the molecules of the body which impart different degrees of elasticity in different directions. As a consequence, the transmitted light wave is divided into two parts, which advance with unequal velocities ; one (*a d c*, Fig. 52) follows the common law of refrac-

Fig. 52.

Double refraction.

Fig. 53.



Double refraction.

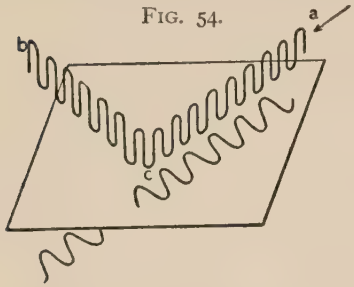
tion, and is called the *ordinary ray*, while the other (*a b*, Fig. 52) does not, and is called the *extraordinary ray*. This may be illustrated (Fig. 53) by placing a crystal of Iceland spar over a black spot or printed matter, and the images will appear double, the ordinary image seemingly nearer the eye than the other. Now, if the crystal be turned around while still lying on the paper, it will be observed that one image (the ordinary) remains fixed in position and the other (the extraordinary) describes a circle around it.

2. Polarization of Light.—According to the undulatory theory of light, the particles of ether through which a ray of light is propagated vibrate in a variety of planes perpendicular to the line of propagation. When this light is polarized, the vibrations of the ether particles take place in a single plane perpendicular to the line of propagation. The unaided eye cannot distinguish between them, but a variety of means exist by which the difference can be demonstrated.

Polarization may be of two kinds, plane or circular, according as the propagating wave is made up of particles vibrating in parallel planes or of those describing circles.

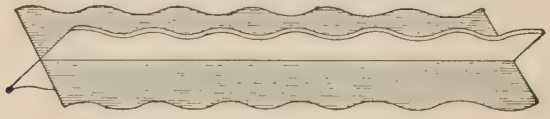
Plane Polarization may be produced by reflection or refraction. (*a*) By *reflection*. When a ray of light falls at an angle on any non-metallic polished surface, such as wood, ivory, unsilvered glass, quartz, etc., it undergoes polarization in the plane of reflection,—that is, all the reflected waves (*c b*, Fig. 54) vibrate in the same or parallel planes ; hence are polarized. The other waves, vibrating in different planes, pass through or are absorbed. The completeness of polarization depends upon the angle at which the ray falls upon the surface. For glass this is 35° 25′. Light is also more or less polarized by reflection from water, from the clouds, and from all objects which aid in diffusing light. (*b*) By *refraction*. It has been shown under double refraction that certain crystals have the power of arranging (polarizing) ordinary light into two rays (ordinary

Fig. 54.



Polarization by reflection.

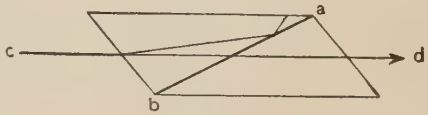
Fig. 55.



Vibrations of ordinary and extraordinary rays.

and extraordinary), which vibrate in planes at right angles to each other, as shown in Fig. 55. One of these rays (the ordinary), which is more retarded in passing through the crystal, may be entirely suppressed and a single polarized ray transmitted by means of what is known as a Nicol's prism. This consists of a rhombohedron of Iceland spar which has been cut through its short axis (*a b*, Fig. 56) and cemented together in the same position with Canada balsam. The light ray enters from *c* and undergoes double refraction, the extraordinary polarized ray passes out at *d*, while the ordinary ray is

Fig. 56.

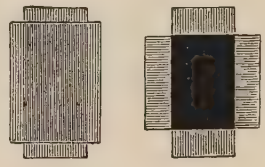


Nicol's prism.

reflected off at the surface of the balsam near *a*. By means of this Nicol's prism we are able to ascertain whether a source of light is polarized or not ; for, on rotating, the light, if polarized, will produce alternately an illuminated or dark field of vision at every turn of 90°. A combination of two of these Nicol's prisms is employed in the polariscope (Fig. 58) : one produces the polarized light, and is called the *polarizer ;* while the other, which is used for examining this light by rotating, is called the *analyzer.*

Plates cut from the mineral tourmaline also serve for polarizing light. Fig. 57 represents two thin plates, which, if so placed that the axes are parallel, will cause polarization of the beam of light that passes through. Now, if the upper plate (the analyzer) is slowly turned, the polarized light passing through is gradually intercepted and becomes feebler until the axes are perpendicular to each other, when total darkness ensues. These may be used for examining polarized light like the Nicol's prism.

FIG. 57.



Tourmaline plates.

Circular Polarization.—If a beam of plane polarized light fall upon a plate of quartz which has been cut at right angles to its axis, two equal beams will be produced plane polarized at right angles to each other. Since the extraordinary ray travels over a longer path through the plate than the other, it is one-quarter of a wave in advance. The resulting motion of the two waves will be circular, like that of a turning corkscrew. Circular polarization may be either right-handed (moving in the direction of the hands of the watch)—called dextrogyrate—or left-handed (moving in the opposite direction)—called lævogyrate. The various systems of polariscopes in use are all based on circular polarization.

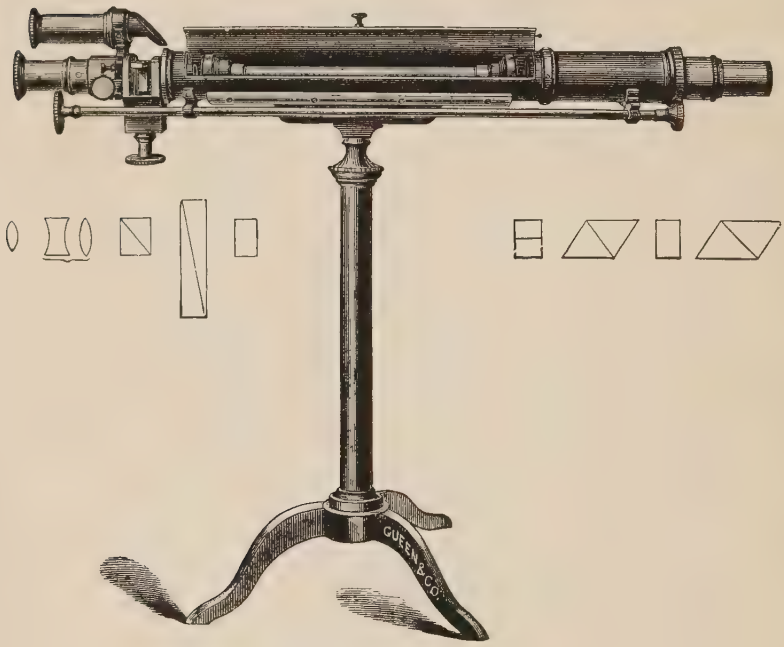
3. Applications of Polarized Light.—By the aid of polarized light we are able to distinguish between minerals or salts of different crystallographic systems, and determine to which a given fragment of a crystal may belong. Thin slices of the crystal in question, if examined between two Nicol's prisms or between the tourmaline plates, will show rings of color in case the crystal belongs to any other than the regular system.

Those belonging to the tetragonal or hexagonal systems show circular rings on which appears a cross, which is black or white

according to the position of the analyzing prism. Such crystals are called *uniaxial.* Those belonging to the orthorhombic, monoclinic, or triclinic systems show elliptical rings on which appear black or white bands or curves. Such crystals are called *biaxial.*

Beautiful colors are produced by the action of polarized light, even when the object is not definitely crystallized. Microscopes are frequently provided with a set of two Nicol's prisms, one under the stage and the other in the eye-piece, in order that the delicate structure of objects can be studied under polarized light.

FIG. 58.



Polariscope.

Many organic substances, as sugars, essential oils, alkaloids, albumin, etc., show a characteristic action upon the ray of polarized light, rotating it circularly to the right (dextro-rotatory) or left (lævo-rotatory). Such substances are said to be *optically active.* The polariscope (Fig. 58) is an instrument based on this principle, and by its aid the strength or purity of these various substances may accurately be determined. The solution

of the substance to be examined, contained in a tube with glass ends, is placed in the instrument between the polarizer (the prism to the right below the figure) and the analyzer (the prism to the left). To the left of the analyzer are the lenses belonging to the eye-piece; to its right are the long quartz wedges of opposite rotatory power. For a description of the various kinds of instruments and methods of operation the reader is referred to special works on this subject.

CHAPTER VI.

MAGNETISM.

I. Magnets, Natural and Artificial.

A certain black mineral (ferroso-ferric oxide, Fe_3O_4) was early known to possess the property of attracting iron or steel. It was known as *magnes*, from the city of Magnesia, in Asia Minor, near which it was first discovered. It was later called *lode-stone*, because of the property of leading or pointing north and south when freely suspended. Fragments of this mineral are now known as native magnets, and the property thus manifested is called magnetism. Native magnets, however, as a rule, have been replaced in experimental work by the smaller and more convenient artificial magnets of steel. Soft iron can also be magnetized, but, as we will see later, is not adapted for permanent artificial magnets, as it does not retain the power as well as steel. These magnets are commonly known by the designations bar magnets, magnetic needles, and horseshoe magnets. The latter have the convenience that because of their shape the two ends of the magnet are near each other, and can be readily covered by a piece of soft iron, known as an armature, which tends to strengthen and preserve the full magnetic power of the magnet. It is found, moreover, that in a steel magnet the magnetic effect does not penetrate very far, so that several bar or horseshoe magnets, separately magnetized and then riveted together, are more powerful than a single magnet of the same size as the compound one.

II. Properties of Magnets.

The most important property possessed by the magnet, either natural or artificial, is the power of drawing to it or lifting up small pieces of iron, such as nails or tacks. Iron is not the only metal thus drawn to the magnet. Nickel and cobalt are also attracted, although in a lesser degree. This influence of the magnet is not dependent upon the presence of air, nor is it hindered by the interposition of solids, like wood or glass. The

attraction takes place in vacuo and through non-magnetic solids as readily as under normal conditions.

Polarity.—A piece of iron is attracted with unequal intensity by the different parts of a magnet. The two ends possess this power in the highest degree, and the middle of the bar or horse-shoe is apparently almost destitute of the power. This is seen to advantage if a bar magnet or needle is dipped into iron filings. Thick bunches of the filings will adhere at either end, while the central part of the bar is practically bare and free from filings The ends of the magnets, or points in which the magnetic power is concentrated, are called the *poles*, and the part of the magnet which seems to be destitute of power is called the *neutral line* Again, if a magnetic needle or bar magnet be suspended freely, we shall find that one pole will always point to the north and the other to the south. Hence we designate one as the *north pole* and the other as the *south pole* of the magnet. On bar magnets they are usually marked N and S, while on the magnetic needle the north pole is usually arrow-pointed.

III. Laws of Magnetism.

1. Attraction and Repulsion.—If the two poles marked N of two bar magnets be brought close to each other, we find no evidence of any attraction, and if, instead of two bar magnets, we take a freely suspended or oscillating magnetic needle and approach its pointed end with the north pole of a bar magnet, we find an actual repulsion,—the north pole of the needle is driven violently away while the two are yet some distance apart. If, on the other hand, the pole of a magnet marked N be approached by the pole of another magnet marked S, the two are attracted, and on touching hold together strongly. In the case of the oscillating magnetic needle, a pole of a magnet will cause the end of the needle of opposite name to swing violently toward the approaching magnet. These observations are summarized in the law of magnetic attraction : *Poles of the same name repel and poles of contrary name attract one another.*

2. Location of the Magnetic Power.—When a steel bar or needle is magnetized, even though the magnetism be effected by rubbing it with one pole of a magnet only, it acquires both north and south polarity, and if this bar be broken in two and the division continued until the pieces are quite small, the same condition exists in each of the fragments. These results are very important as giving us some idea of the nature of the magnetic

influence. It undoubtedly resides in the molecules themselves, each of which must be supposed to have been given magnetic polarity when the bar or needle was magnetized. Therefore no mechanical subdivision can rob them of this property. At the same time the strong manifestation of the magnetic power at the two ends, and the existence of a neutral line for the time being in the middle of the bar, shows that the force is cumulative in either direction, and it is wanting in the middle of the bar because the forces temporarily neutralize each other there.

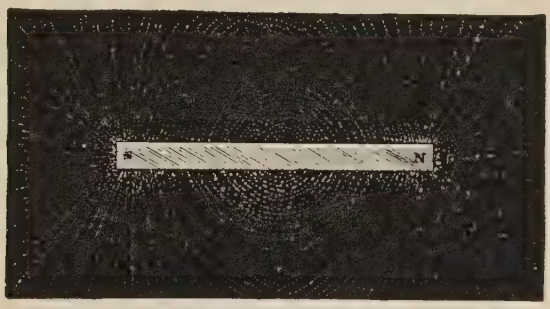
3. **Magnetic Induction.**—A piece of soft iron brought close to a strong magnet is affected by it more strongly than appears in the simple attraction. While under the influence of the original magnet it becomes a magnet itself, and is capable of attracting and repelling another piece of iron, according to the laws of magnetic attraction. This is due to what is termed *magnetic induction*. The end of the piece of iron next to the inducing magnet is given a polarity the opposite of that possessed by the pole exerting the influence, while the end of the iron farthest from the inducing magnet shows a polarity the same as that of the pole with which the iron is in contact. This induction takes place through glass or paper or other non-magnetic substance, without appreciable loss.

The influence in the case of iron is only temporary, and when detached or removed from the inducing magnet it loses its power at once. In the case of steel, on the other hand, this power is not immediately or wholly lost on detaching it from the inducing magnet. This is due to the fact that while steel has considerable magnetic retentivity, or coercive force, soft iron has very little. Hence permanent magnets are made of steel, while, as we will see later (see p. 130), electro-magnets are made of soft iron.

4. **Lines of Magnetic Force.**—If a bar magnet be laid upon a horizontal surface like a table and covered by a glass plate or a sheet of card-board, upon sifting over the glass or card-board fine iron filings we will find that they arrange themselves in peculiar curves, as illustrated in Fig. 59. These are known as the *lines of magnetic force*, and indicate the lines in which the influence of the magnet is felt. It will be noticed that they seem to radiate out from the neighborhood of the two poles, and that the curved lines from the two poles join and make a series of circles enclosing the neutral line of the magnet. These curves thus formed by the iron filings, however, do not indicate that the magnetic force is felt in narrow lines only, but they mark its direction. The entire

space around each of the poles is permeated by this influence, and is, therefore, known as the *magnetic field*. The strength

FIG. 59.



Magnetic curves.

of the attraction within this field is governed by a law of distance similar to those already noted under heat and light. It is expressed as follows: *Magnetic attraction or repulsion varies inversely as the square of the distance through which it acts.*

IV. THE EARTH AS A MAGNET.

1. The Influence of the Earth upon Magnets.—We have already seen that a magnetic needle if freely suspended will always, after oscillation, come to rest in a position pointing north and south. We will also find, if the needle be suspended so that it can swing in a vertical plane, that as we move from the equator toward the pole the needle will dip increasingly, and near the pole it assumes a vertical position. These two results we attribute to the earth's influence. We have effects analogous to these if a powerful bar magnet be laid upon a table and we hold suspended over it by a fine thread a delicate magnetic needle. The latter, as it approaches the large magnet, immediately assumes a position parallel to it, and as we proceed from the neutral line of the large magnet toward the pole the small needle dips toward the pole approached, and when immediately over it assumes a vertical position. If over the south pole of the large magnet, it is the pointed or north end of the needle which dips down, and, if over the north pole of the magnet, it is the unmarked or south end of the needle.

2. The Earth Itself a Magnet.—We are led by the analogy just stated to consider that the earth itself acts as a great magnet,

and that it is to its directive influence that the oscillating needle always tends to assume the north-and-south direction. If the earth be considered to act as a magnet, we should be able to locate its poles. These *magnetic poles* of the earth were, in fact, discovered by the navigator, Sir James Ross. The north magnetic pole was found on the western coast of Boothia in 70° north latitude, and a point in the South Sea was found where the inclination or dip of the needle was 88° 37′, whence the position of the south magnetic pole was calculated to be in about 75½° south latitude. It will be seen that the magnetic poles of the earth do not agree in position with the geographical poles. Hence the needle does not in most places point due north and south or in a line determined by the north star. The angle which the needle makes with the geographical meridian is known as the *angle of declination.* It is found that this angle differs at different places, and that for any one place it changes slightly from year to year. The magnetic axis of the earth, in fact, is slowly oscillating.

V. Applications of Magnetism.

Permanent magnetism has few applications compared with those that have been found for electro-magnets. These will be noticed farther on. The most important application of permanent magnets is in the *mariner's compass.* In this the freely oscillating magnetic needle is mounted in such way that under the influence of the earth's directive action it is made to indicate the direction in which a ship is moving. For this purpose one or more magnetic needles are attached to the under surface of a circular disk of card-board or mica, upon the upper surface of which are marked the thirty-two points of the compass. This disk is supported upon a delicate pivot moving in an agate cup, so that it responds to the slightest change of course of the ship. With the general introduction of iron and steel ships the use of the compass would seem to be attended with great difficulty, because of the local attraction for the needle. It has been found possible, however, to correct for this local influence so as not to interfere with the accuracy of the directive action of the needle. The compass is supposed to have been known to the Chinese long before its introduction into Europe in the twelfth century.

Permanent magnets, as well as electro-magnets, are also used in separating magnetic iron ore from accompanying sand and crushed rock material, and in picking out small particles of scrap iron from malt and grain before crushing.

CHAPTER VII.

ELECTRICITY.

ELECTRICITY is known to us only by its effects and various manifestations. Like energy, it can neither be created nor destroyed, but is capable of being moved from one place to another and put under stress. In some of its deportments it is like an incompressible fluid pervading all space, in others a highly attenuated ether, and, if not identical, it is closely related to luminiferous ether. According to Maxwell, light itself is an electric phenomenon and light waves are electro-magnetic waves. The importance of electricity may be measured by the fact that an expenditure of energy of one kind (mechanical or chemical) can be made to reappear as electrical energy readily convertible into heat, light, or other useful form of energy.

According to its methods of production and various manifestations, electricity will be considered under the following heads, —namely, *static*, *dynamic*, *thermal*, and their practical applications.

A. STATIC OR FRICTIONAL ELECTRICITY.

Thales of Miletus (500 B.C.) was probably the first who mentioned that when amber is rubbed it acquires the property of attracting light bodies, such as bits of paper, feathers, pith balls, etc. It was not until the sixteenth century that Dr. Gilbert, an English physician, showed that many other substances, as sulphur, resin, shellac, glass, rock-crystal, etc., possess like properties with amber. He applied the name *electrics*, from ἤλεκτρον (elektron), the Greek name for amber, to all such substances.

1. Conditions of Production.—If a stick of sealing wax, sulphur, or hard resin be rubbed briskly with a piece of flannel, it will acquire the property of attracting light bodies, like slips of paper, feathers, pith balls, etc. A glass tube carefully dried and rubbed with a silk handkerchief will show similar phenomena. In a dark room the bodies so rubbed often appear slightly luminous, and sparks are sometimes given off when they are touched. It is evident that these are manifestations of a new form of energy

developed by the friction of the two bodies and distinct from heat, which may be developed at the same time. The generally received explanation of this change of energy into a new form is that friction and the other means referred to disturb the neutral condition in which the molecules of bodies ordinarily exist, and develop therefrom two opposing influences, which then give us the so-called "electrical" phenomena. These influences may be designated as *positive* and *negative*, or *vitreous* and *resinous* electricity.

The development of electricity of either kind in a body is said to give it a certain *potential* as compared with another body, either electrified or unelectrified. A body charged with positive electricity is said to have a positive potential, while a body negatively charged has a negative potential. These opposing charges may be equal, in which case, when the two bodies are brought into contact, they neutralize each other and leave the bodies unelectrified, or they may differ in potential, in which case a residue remains of the stronger charge.

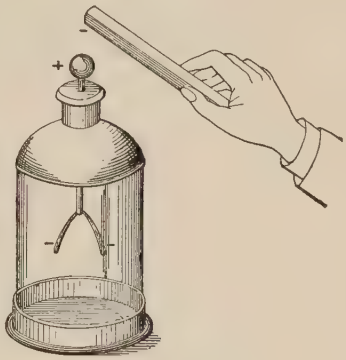
If instead of rubbing resins or glass we rub metals with flannel or silk, apparently no electrical effects are produced. This want of electrical excitement is, however, only apparent. If a metal tube is provided with a glass handle by which it may be held and is then rubbed with silk or flannel, it becomes charged with electricity. Its seeming inability to become electrified is due to the fact that it is a *conductor* of electricity, and hence the charge passes off rapidly into the hand or the object with which it was in contact. We may, therefore, distinguish two classes. *conductors*, like metals, water and aqueous solutions, plants and animals, and *non-conductors*, like silk, glass, resins, rubber, and dry air. Non-conductors are also often called insulators, as they prevent the loss or dissipation of a charge of electricity accumulated upon a conductor. Glass and hard rubber are thus used in practice. We can now somewhat understand the result attained when a stick of shellac is rubbed with a piece of flannel. Both become electrified, the shellac taking the negative charge of electricity and the flannel the positive charge. On the other hand, when glass is rubbed with silk, both likewise are electrified, but the glass takes the positive electricity and the silk the negative electricity. Both these results are, however, explained if we arrange the substances referred to consecutively in what is known as a potential series. In this list the substances are named in such order that any one becomes positively electrified when rubbed

with one of the bodies following, but negatively when rubbed with one of those which precede it :

1. Cat's skin.
2. Flannel.
3. Ivory.
4. Rock-crystal.
5. Glass.
6. Cotton.
7. Silk.
8. The hand.
9. Wood.
10. Metals.
11. Caoutchouc.
12. Sealing-wax.
13. Resin.
14. Sulphur.
15. Gutta-percha.
16. Gun-cotton.

2. Laws of Electrical Attraction and Repulsion.—In order to ascertain whether a body is electrified or not we employ either the *electric pendulum* or *electroscope** (Fig. 60). By means of these we are also able to distinguish between positive (+) and negative (—) electrification. If a warm dry glass tube be rubbed with a piece of silk and then presented to the electrical pendulum, which consists of a pith ball suspended by a silk thread, it will be attracted at first, whereby it receives a positive charge from the glass, then, almost immediately afterwards, the ball is repelled, since it has become charged with the same kind of electricity as the glass. If now a stick of sealing-wax be excited with a piece of flannel and be brought near to the

FIG. 60.



Electroscope.

* The gold- or silver-leaf electroscope is far more sensitive than the pith ball. It consists of a glass jar closed at the top with a cork through which passes a metallic rod surmounted with a ball of metal, and at the lower extremity are attached two gold- or silver-leaf strips. The jar itself is covered with a non-conducting varnish. If an electrified body is brought *near* to the ball of the electroscope, the former acts on the latter by induction, attracting the opposite kind of electricity into the ball and repelling the same kind (as the excited body) into the gold-leaves, both of which, being charged alike, will diverge. To ascertain the *kind* of electricity in a body, the electroscope is electrified with the body in question, then with the finger touch the top knob while the leaves are diverging, and remove the finger before taking away the exciting body. When this latter has been removed, the electricity retained in the ball spreads over the rod and leaves, causing them to diverge. Now excite a glass rod (+) with a piece of silk and let it touch the electroscope ball; if the leaves diverge more, their charge was positive and that of the body in question was negative; if the leaves collapse, the body must have been charged positive.

charged pith ball, the latter is attracted to the former because the wax is negatively charged. From these experiments we will observe that unelectrified bodies are attracted by electrified ones, and that when both are charged with the same kind of electricity repulsion takes place ; when the charges are of opposite kind attraction results.* The laws of electrical attraction and repulsion are as follows :

1. Electrical charges of like name repel each other ; electrical charges of opposite name attract each other.

2. The force with which each of the two charges attracts or repels the other is directly proportioned to the product of the two quantities of electricity and inversely as the square of the distance between them.†

3. Electrification by Influence.—A body charged with either positive or negative electricity will exert an influence upon unelectrified bodies in the neighborhood and decompose the neutral condition existing in them, attracting to the surface next to the electrified body a charge the opposite to that which it contains (see Electroscope, Fig. 60). At the same time the decomposition of the neutral condition sets free both kinds of electricity, and while one is drawn towards the original electrified body, the other is driven towards the farther extremity of the body which comes under its influence. Such action is called *induction*, and by its means a body once electrified by friction is capable of exerting an influence upon surrounding bodies and developing in them corresponding charges. If this induced electricity is drawn off by suitable conductors and the body again presented in the neutral condition, fresh inductive action will develop fresh charges, and in this way notable charges of both positive and negative electricity can be accumulated. The various newer forms of frictional electrical machines are based upon the principle of repeated induction developing anew fresh electrical charges.

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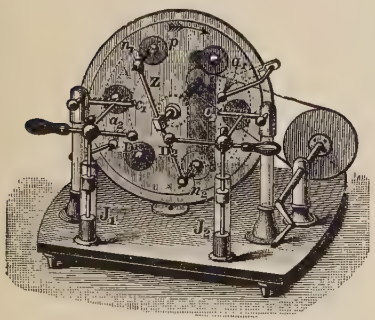
* The electrical charge of a pith ball or electroscope may be removed by touching with the finger, provided it is not within the influence of an electrified body.

† In the first case, if we have one body given a charge of 2 and another one of 3, the force between them will be $3 \times 2 = 6$ times as great as if each had a charge of 1. In the second case, if two small electrified bodies 1 centimeter apart repel each other with a certain force, and this distance be increased to 2 centimeters, the force exerted will be only ¼ as great, and at 10 centimeters it will be only $\frac{1}{100}$ part. This law of inverse squares is true for small bodies only.

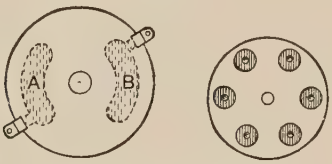
4. Electrical Machines.—In the older forms of electrical machines we have simply a circular plate or hollow cylinder of glass, which is rotated rapidly while pressing against pads of silk or leather. These latter are coated with an amalgam or with a bronze powder (stannic sulphide), and by their friction with the glass develop electricity. The plate becomes charged with a positive electricity, which is taken off by a metallic comb and accumulates on a brass knob known as the prime conductor, while the pad which presses on the glass plate receives a negative charge which accumulates on a second insulated metallic conductor. A spark may now be taken from either of the insulated conductors. If, however, the conductor which received the negative charge be "grounded,"—that is, connected with the floor or table by a metallic chain,—the potential of the positive conductor becomes greater, and longer sparks can be taken from it. A newer and more powerful form of frictional machine is the Toepler-Holtz (see Fig. 61), which is in reality a combination of two induction machines. On the back of a stationary glass

FIG. 61.



Toepler-Holtz electrostatic machine.

FIG. 62.



Back fixed disk with field plates on back.

Front rotating disk with carriers on front.

plate are two cards, A and B, which act as inductors, and on a smaller revolving glass plate in front of the former are pasted a series of tin-foil carriers (see Fig. 62), each of which has in its centre a button designed to serve as a contact. A stationary metal rod, z, crosses diagonally in front of the moving plate, and to this are attached flexible wire brushes, n_1 n_2. As the movable glass plate revolves, these brushes touch the two tin-foil carriers, which are at diagonally opposite positions on the plate, and remove the induced charges from them. As these carriers come around in front of the inductor cards they touch

metallic brushes, C_1 C_2, which make contact with the inductors through metallic rods and thus recharge them with positive and negative electricity respectively. The cards then act inductively upon the revolving glass plate again and communicate to it fresh quantities of the two forms of electricity to be taken up by the brushes of the diagonal rod. The metallic conductors attached to the stationary plate terminate in knobs, D_1 D_2, between which a discharge of sparks is kept up while the other plate is in revolution. These conductors are provided with insulating handles of hard rubber, and are made to slide in and out of metallic sockets, so that the distance between the discharging knobs can be lengthened or shortened according as the difference of potential between the positive and negative charges becomes greater or smaller. The discharging knobs, D_1 and D_2, communicate also with two small Leyden jars, J_1 and J_2, the purpose of which is to accumulate the charges before any discharge takes place. Without them the discharges between the knobs of the prime conductors are continuous and short, while with them the sparks are longer, more brilliant, and louder.

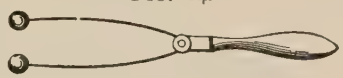
5. Electrical Condensers.—If two metallic surfaces be brought near to each other and yet be kept apart by some insulating medium, we may, by charging one with either positive or negative electricity, cause a charge of opposite name to accumulate in the other by induction. Hence such a combination is called an electrical accumulator, or condenser of electricity. The simplest form would be a pane of glass coated on either side to within an inch of the edge with sheets of tin-foil. More generally a glass jar is used, and this is coated within and without with tin-foil for about two-thirds of its height. Through a cork or wooden cap passes a metal rod terminating above in a knob and ending below in a metallic chain which is long enough to touch the inner tin-foil on the bottom of the jar. Such a jar is known as a *Leyden jar*. It may be charged by grasping it in the hand around the side and then holding the projecting knob to one of the prime conductors of the electrical machine. This charges the inner coating with that kind of electricity which had accumulated on the prime conductor, and at the same time the outer coating by induction takes a charge of the opposing kind. The jar may then be placed upon a table and the charges will remain with little loss

FIG. 63.

Leyden jar.

for quite a length of time, but if contact is made between the inner and the outer coatings by a metallic conductor or through the body, the two opposing electricities at once unite and the jar is discharged. The charge of the Leyden jar resides on the outside and inside surfaces of the glass and not on the metallic coating. This may be proven by means of a dissected jar, as shown in Fig. 65, in which two tin cups serve as substitutes for the outer and inner coating of tin-foil. When the cups are in place the jar is charged and set on an insulated surface (glass or rubber), then the inner cup with hook is removed, and by inverting the glass tumbler is removed from the outer tin cup. It will be found on testing with a pith ball that the two surfaces of the glass are oppositely electrified, while no trace exists on either of the two tin cups. On putting together again the jar will be found to be still highly charged. When a Leyden jar is heavily charged, care must be taken in handling, to avoid touching the knob with one hand while holding with the other, as the shock experienced is very severe.

Fig. 64.



Leyden jar discharger.

Fig. 65.

Dissected Leyden jar.

6. Electrical Discharge and its Effects.—The effect of the spark discharge depends very much upon the nature of the body through which the discharge takes place. Its mechanical effects are seen most readily in the case of bad conductors. These are often shattered. Thus it is possible to pierce card-board or leather readily with the aid of the discharge from the Holtz machine. A glass plate may also be pierced in this way. The discharge of atmospheric electricity during a thunder-storm, as seen in the lightning flashes, however, gives us the mechanical effects on the grandest scale. The thunder-cloud and the earth constitute the two parts of a huge condenser. When the difference in potential has become sufficiently great to cause the discharge to take place through the intervening air, we have the lightning stroke which rends the tallest trees as well as buildings which stand out prominently or in exposed positions. Protection against this lightning discharge is sought in the case

of tall edifices by the use of metallic conductors, which, while insulated from the building, are connected with the ground.

The physiological effects of the spark discharge consist in sudden vibrating shocks felt in the arm or elbow when a Leyden jar is discharged through the person, and in a sharp prickling sensation felt on the knuckles or fingers when the prime conductors of a plate machine are touched. With large jars or a strong induction machine the spark discharge may be quite dangerous. As will be seen later, this peculiar physiological effect belongs to the spark discharge, whether from the friction machine, the Leyden jar, or the secondary current of the induction machine, because in all these cases the electricity is manifested under high difference of potential or tension.

The luminous effects of a spark discharge vary with the potential of the two electricities and the medium through which the spark passes. Thus, in ordinary air the spark is white and brilliant, in rarefied air it is reddish, and *in vacuo* it is violet. Rarefied gases, like hydrogen, nitrogen, and carbon dioxide, also cause the spark to show in different colors. This subject will be more fully discussed under Induction Currents (see p. 140).

The heating effects of the spark discharge are also easily recognized. The spark passed through inflammable liquids, like alcohol or ether, inflames them ; the spark will ignite ordinary illuminating gas, as is seen in many forms of domestic gas-lighting apparatus ; when the spark is passed continuously through a metallic wire, although relatively a conductor the wire still becomes heated. Magnetic effects are also observed. A steel bar or needle may be magnetized if placed inside a tube around which is coiled a wire, through which the spark discharge is made to pass. We will see later, under Voltaic Electricity, that powerful electro-magnets are made in an analogous manner.

Lastly, the chemical effects of the spark discharge are the effecting of chemical decompositions and recombinations of the elements. Thus, if the spark is passed for a time through dry ammonia gas, it is decomposed into hydrogen and nitrogen. On the other hand, the spark discharge will cause the union of hydrogen and chlorine or hydrogen and oxygen when admixed as gases. Among chemical effects must also be noticed the ozonizing of the oxygen of the air through which the discharge takes place. This is readily recognized by the odor which is always noticed in the neighborhood of the plate electrical machine. A fuller mention of this production will be found under Ozone.

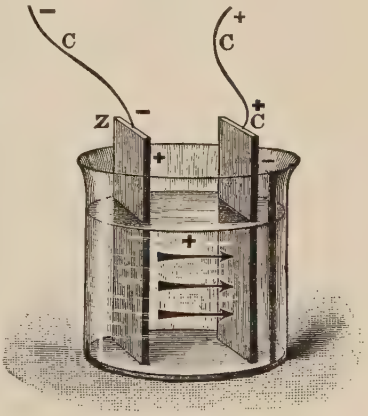
B. Dynamic Electricity.

The electricity hitherto spoken of is known either as *static electricity*, because it remains, when collected, upon the object charged, or electricity of *high tension*, because it accumulates upon neighboring conductors until a high tension or difference of potential is reached, when it is discharged by the passage of the spark. Differing from this in its form and manifestations, although not in identity, is *dynamic* (from *δύναμις* = *power*), or electricity of chemical action, so termed because of its various manifestations of power. Synonymously we also employ the terms *galvanic*, *voltaic*, *current*, and *chemical* electricity. Under this general heading *magneto-* and *thermo*-currents will be considered.

Galvani, an Italian, was the first (1780) to discover this new method of generating electricity, and Volta the first to construct a battery, known as Volta's Pile, which consisted of a series of alternate zinc and copper plates placed one above the other and separated by felt moistened with brine.

1. Simple Voltaic Cell or Couple.—After a century of constant experiment, scientists still employ the same metals and arrangement in series as Volta, only superseding the moist felt with a fluid. If a plate of zinc, z (see Fig. 66), and one of copper, c, are dipped in dilute sulphuric acid, bubbles of hydrogen gas will collect on the surface of the zinc, which after a time gradually disappear. If we now connect the two plates by means of a wire, the chemical action becomes more violent and a greater amount of hydrogen is liberated ; but this time it is disengaged at the surface of the copper instead of the zinc. The latter serves as fuel for generating, while the former collects the current. The production of a current in this case is entirely due to the chemical action which ensues when two dissimilar metals are moistened with the same fluid, one metal being more susceptible to the action of the fluid

Fig. 66.



Simple voltaic cell.

than the other. If the two wires attached to the plates be separated, electrical action ceases; if they are brought near enough together in the dark, a small spark is seen to pass between them. The joining of the two wires—that is, the establishment of communication between the metals of a battery—is called *closing the circuit;* the separation of these, *breaking* or *opening* it. The metal which is the more energetically acted on by the liquid (in this case the zinc) is called the *generating* or *positive* plate, while the other (the copper) is the *conducting* or *negative* plate. The current passes through the liquid from the zinc to the copper, and above through the wires from the copper to the zinc, thus forming a complete circuit. The ends of the wires, C C, leading from the plates are called the *poles* or *electrodes;* the one connected with the zinc, or generating element, is called the *cathode* or *negative* (—) *pole*, while that of the copper, or conducting element, is the *anode* or *positive* (+) *pole.*

2. **Electro-motive Series.**—As already stated, a current results when two different metals are placed in a fluid which acts on one more strongly than the other. The generating plate is of higher *potential** while the collecting plate is of lower potential. This difference of potential produces *electro-motive force,** which varies between different metals. Various metals have been arranged in a series which expresses their relations to one another in this respect. Such a table is called the electro-motive force series.

+ 1. Zinc.	5. Iron.	9. Copper.
2. Cadmium.	6. Nickel.	10. Silver.
3. Tin.	7. Bismuth.	11. Platinum.
4. Lead.	8. Antimony.	12. Graphite (gas carbon) —.

These elements are arranged with the electro-positive at one

* *Potential,* in the physical sense, is that condition of matter by virtue of which it is capable of exerting physical force. Thus, a body of water may, by the expenditure of a definite amount of energy, be forced to some height into a reservoir. This mass of water, by virtue of its position, retains the same energy which has been expended upon it. It has acquired the power to do work; it possesses potential energy. As this water in returning to its former state of equilibrium flows from a higher to a lower level, so electricity flows from bodies of a higher to those of a lower potential. We measure the heat potential of a body by the effect it can produce on temperature, the electrical potential of a body by the electrical force or pressure it is capable of exerting. This force or power which tends to move electricity from one place to another, due to a difference of potentials, is called the *electro-motive force* (E.M.F.). The unit of E.M.F. is the volt, which represents the power of a current to overcome resistance.

end and the electro-negative at the other. If any two of these be placed in dilute acid, the current will pass from the lower to the higher (number). Thus, iron is electro-negative to zinc and positive to copper, while silver is negative to zinc and positive to platinum. The E.M.F. is greater in proportion as the metals are distant from each other in the series ; for this reason batteries of zinc and platinum (or carbon) give the greatest electro-motive force.

3. Local Action and Polarization.—Zinc when placed in water decomposes it, forming zinc oxide, and hydrogen is set free. This action is of very short duration, owing to the coating of the metal with an insoluble film of oxide. The employment of dilute sulphuric acid obviates this by dissolving the oxide as rapidly as it is formed, leaving the surface free. Chemically pure zinc does not react with dilute sulphuric acid until the circuit of the battery is closed. Commercial zinc, which is very impure, reacts constantly with the acid, whether the circuit is open or closed ; hence a great waste takes place without contributing anything to the quantity of electricity generated. The presence of these impurities, which usually consist of iron, lead, cadmium, etc., induces the generation of local currents independent of the copper, because these metals are electro-negative to the zinc. This waste of local action may be prevented by *amalgamation*, which consists in rubbing the surface of the zinc plates (which have been cleaned with soap and dilute acid) with mercury.

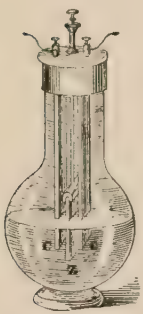
Polarization is a troublesome feature of the simple voltaic cell. It is due to the accumulation of a film of bubbles of liberated hydrogen over the surface of the copper plate. As this increases, the current weakens and finally ceases. The chief cause of this weakening of the current is the setting up of an opposing electro-motive action, for the hydrogen gas is electro-positive to the copper, and tends to start a current in the opposite direction to the regular one. To avoid this polarization it is necessary to suppress the accumulation of hydrogen. This is usually accomplished by chemical means, which consists in introducing into the cell some substance that possesses a strong chemical affinity for the hydrogen, thereby removing it without interfering with the working of the cell. The various means whereby this is accomplished will be explained under the individual cells, which, in view of this, are divided into two general classes,—namely, one- and two-fluid.

4. Voltaic Batteries.

ONE-FLUID CELLS.—Though simpler than the two-fluid cells, these are subject to polarization to a greater or less degree. However, if allowed to rest at frequent intervals, they rapidly regain their original strength. These one-fluid batteries are especially adapted for "open-circuit" service, such as electric bells, signal circuits, etc., where the current is only required momentarily.

The Bichromate Cell.—A convenient form is known as the Grenet Dip Battery (Fig. 67). This consists of two carbon plates, C C, with a zinc, Z. This latter is attached to a sliding rod, so that it can be raised out of the fluid when not in use. The exciting fluid consists of potassium bichromate (9 parts), sulphuric acid (25 parts), and water (66 parts). Polarization is prevented through the reducing action of the liberated hydrogen on the chromic oxide.*

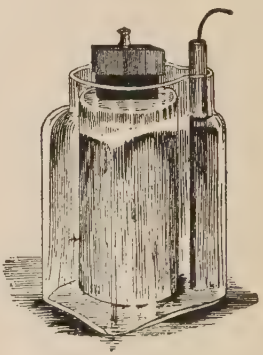
FIG. 67.



Bichromate cell.

The E.M.F. of this cell is about 2 volts. It loses in intensity when used for long periods, but regains it when allowed to remain out of action for a time.

FIG. 68.



Leclanché cell.

The Leclanché Cell (Fig. 68).—This consists of an inner porous earthen cup which contains a carbon plate packed in fragments of coke and manganese dioxide. The top is covered with a layer of pitch. The positive plate is a rod of zinc, which dips in an exciting fluid consisting of a saturated solution (6 ounces to a quart jar) of sal ammoniac contained in the outer glass jar. Through the action of the salt on the zinc a double chloride of zinc and ammonium is formed, while ammonia and hydrogen gases are liberated at the carbon pole. The hydrogen combines with the oxygen evolved by chemical action from the depolarizer

* The chemical action in the exciting solution is $K_2Cr_2O_7 + 7H_2SO_4 = 2CrO_3 + K_2SO_4 + H_2O + 6H_2SO_4$. When in action it is as follows:

(a) $3Zn + 3(H_2SO_4) = 3ZnSO_4 + 3H_2$.

(b) $2CrO_3 + 3H_2 = Cr_2O_3 + 3H_2O$.

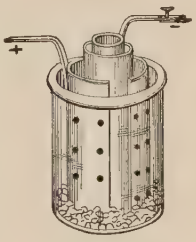
(c) $Cr_2O_3 + 3(H_2SO_4) = Cr_2(SO_4)_3 + 3H_2O$.

(manganese dioxide), and forms water. If electric action is continued for too long a time, excessive quantities of hydrogen collect and polarization ensues, for the oxygen is not developed with sufficient rapidity; hence short periods of rest are necessary. The great popularity of this cell may be judged from the variety of forms in which it appears on the market. It does not require renewing for months, or even years. The E.M.F. of this cell is about 1.47 volts. Other kinds of one-fluid cells are the Smee, Wollaston, and mercuric sulphate batteries.

Two-Fluid Cells.—These are known as "closed circuit" or "constant" batteries, because of the constancy of their action when in continuous use, such as is required in telegraphy, electroplating, etc. In these batteries the conducting element (copper, platinum or carbon) is immersed in a fluid which is capable of suppressing the hydrogen, while the soluble element (zinc) is surrounded by a fluid capable of combining with it.

The Daniell Cell (Fig. 69).—This is one of the oldest and best two-fluid cells in use. The outer glass vessel contains a solution of copper sulphate kept saturated by adding some crystals of the salt. In this is placed a perforated cylinder of copper. Inside of this cylinder is set the porous earthenware cup containing dilute sulphuric acid and a small cylinder or rod of amalgamated zinc. The chemical reaction, when in use, is as follows. Hydrogen is liberated by the oxidation of the zinc, and passes through the porous cup to the copper sulphate solution, which it decomposes into metallic copper and sulphuric acid. The former is deposited on the copper element, while the latter passes to the zinc to replace that already consumed in forming zinc sulphate. This reaction with the current will continue as long as the outer vessel is provided with copper sulphate. The hydrogen is thus entirely suppressed and depolarization is complete. The E.M.F. of this cell is 1.05 volts. The Meidinger and Crowfoot cells are modifications of this.

Fig. 69.

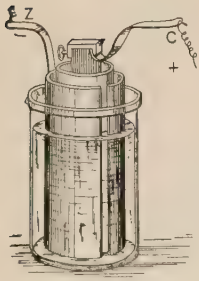


Daniell cell.

The Bunsen Cell (Fig. 70).—This consists of an amalgamated zinc cylinder immersed in dilute sulphuric acid contained in a jar. Within this is a porous cup containing a rod of hard gas carbon immersed in strong nitric acid. The "Grove" cell differs from this only in the replacement of the carbon by a strip of platinum. The hydrogen liberated by the zinc passes through

the cell and unites with a portion of the oxygen of the nitric acid, forming water and decomposing the acid. The production of fumes (N_2O_4) is the chief objection to this excellent and powerful cell. The E.M.F. is 1.93 volts.

Fig. 70.



Bunsen cell.

5. Electrical Units.—When electricity is passing, even though it be through what we call a conductor, it meets with resistance.* For purpose of comparison it is desirable to have a uniform method of measuring this. The unit of resistance is called the *Ohm*, and is the resistance of a column of pure mercury, having a section of one square millimeter and a length of 106.28 centimeters, at a temperature of 0° C. For convenience, coils of wire with a known resistance in ohms are used. These are known as resistance coils, and are prepared in sets, so that any resistance within quite wide limits can be measured with their aid. It is by such means that the location of a break in the ocean telegraph cables can be ascertained so that the cable may be grappled for and repaired.

The unit of current strength is called the *Ampère*. It is the rate of flow of a current which, under the electro-motive force (pressure) of one volt, flows through a circuit which offers a resistance of one ohm. An ampère of current will deposit 0.327 milligramme of copper a second, or 1.177 grammes per hour. The current is also often measured by the amount of hydrogen and oxygen liberated within a given time by the electrolysis of water.

The pressure or difference of potential which causes the electricity generated in a battery or cell to overcome the resistance of the circuit and so effect its passage is called its electro-motive force. The unit of electro-motive force is called the *Volt*. It is the pressure required to maintain a current of one ampère

* Various metals differ materially as conductors: thus, silver is the best, and is followed in order by copper, aluminum, zinc, brass, iron, etc. The better the conductor the less the resistance. Again a difference in dimensions of a given conductor offers differences in resistance; for example, taking two round copper wires of the same diameter, one 100 feet in length will offer *twice* as much resistance as will one of 50 feet. If we have two round copper wires each 50 feet long, and one has twice the diameter of the other, the smaller one will have *twice* the resistance. So the greater the length the greater will be the resistance, and the greater the diameter the less the resistance.

through a resistance of an ohm; practically, it is represented by the E.M.F. of the Daniell cell.

The instruments employed for measuring the ampèrage and voltage of currents are called *ammeters* (ampère-meters) and *voltameters*, and are explained on p. 132. The relation of these three units is expressed in Ohm's law. The Current (in ampères) is equal to the Electro-motive Force (in volts) divided by the Resistance (in ohms). Any two terms being known, the third can be calculated; for, if

$$C = \frac{E}{R}, \text{ then } E = C \times R \text{ and } R = \frac{E}{C}.*$$

6. Battery Formation.—A number of voltaic cells may be coupled together for the purpose of increasing the quantity and intensity of the current. Such an arrangement is called a *voltaic battery*. The coupling may be effected in several ways. Two methods, however, demand attention,—namely, the *series* and *parallel* couplings. When joined "in series," each zinc is joined to the copper or carbon of the next cell, and so on to the end of the line, the one terminal being a zinc and the other a carbon or copper plate: thus, . Series coupling does not increase the rate of current flow (*ampèrage*) more than that of a single cell, while the electro-motive force (pressure in *volts*) yielded increases with the number of cells. When joined "parallel," all the zincs are coupled together and all the coppers or carbons together. They are said to be joined for *quantity* . This arrangement does not give any greater E.M.F. (voltage) than one cell, for the conditions are as though we had but one huge cell with very large zinc and copper (carbon) plates. However, a greater flow of

---

* Examples:

1. What will be the resistance of a conductor through which a current of 5 ampères is passing under a pressure of 30 volts?

$$R = \frac{30}{5} = 6 \text{ ohms.}$$

2. How many ampères will flow through a conductor having a resistance of 10 ohms, under a pressure of 110 volts?

$$C = \frac{110}{10} = 11 \text{ ampères.}$$

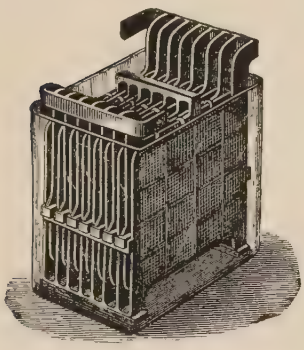
3. How many volts of pressure will be necessary to force 10 ampères through a resistance of 2 ohms?

$$E = 10 \times 2 = 20 \text{ volts.}$$

current (*ampèrage*) is obtained, according to the number of cells introduced.

7. Accumulators, Secondary or Storage Batteries (Fig. 71).—In these the electrical energy furnished is due to an expenditure of chemical energy within the cell. Chemical energy, and not electricity, is stored. The form of accumulator more commonly in use is made by filling the openings of two leaden grids with a paste of red lead (Pb_3O_4) and dilute sulphuric acid. When this has hardened, the plates are placed in a vat of acidulated water and a dynamo current is passed through, the direction of which is changed from time to time, until the red lead on the anode plate has been converted into a semi-porous film of brown peroxide (PbO_2), and that on the cathode plate has assumed a state of spongy metallic lead (Pb). We now have two *different* elements (PbO_2 and Pb), which may be coupled with others, if desirable, and placed in a container with dilute sulphuric acid as excitant. A layer of felt may be placed between the grids. The chemical reaction that takes place during the discharge is the transferrence of one atom of oxygen from one plate (PbO_2) to the other (Pb), whereby lead oxide (PbO) is produced; and as soon as both plates are alike (PbO) the current ceases. The sulphuric acid present converts the lead oxide of both plates into lead sulphate. The plates are recharged by immersing in acidulated water and passing the current through in alternate directions, whereby the lead sulphate is reconverted into lead peroxide and spongy lead with liberation of sulphuric acid. The E.M.F. of these single cells of two plates is about 2 volts. In these secondary batteries, as in the primary, the potential difference (E.M.F.) of a cell does not depend on the size of the plates, but on their nature and that of the exciting fluid.

Fig. 71.



Accumulator.

The cheap *Dry Cell*, which has become popular for running electric bells and circuits, is based on that of Obach, which consists of an outer cylinder of zinc, which serves as a case. This is lined inside with a layer of plaster of Paris, saturated with

sal ammoniac, kept separate from the inside contents by a layer of paper. The core, or central portion, contains a carbon cathode embedded in a mixture of manganese dioxide (MnO_2) and ground retort carbon.

8. Effects of Current Electricity.—The main distinctions between the frictional current or discharge and the current developed by voltaic action are in tension or difference of potential and in amount of the current. Frictional electricity is of high tension but small in total amount, while the voltaic current is of low tension but greater in amount as measured in ampères. Hence the effects will differ somewhat. The mechanical effects of voltaic electricity are very slight as compared with those of frictional electricity. The physiological effects are also, as a rule, very much milder than those of the spark discharge. The wires from a voltaic battery of a dozen cells may be held in the hands without appreciable shock, but a tingling sensation is felt from very strong currents, and prolonged contact with the wires has an exciting effect upon the nerves. The heating effects are dependent, of course, upon the resistance which the circuit offers to the passage of the current and to the amount of current passing. With good conductors like copper, of sufficient section, the heating effect is slight; with wires of insufficient section, or with poor conductors, like platinum, iron, or German silver, the resistance becomes relatively great and the wire becomes strongly heated. It is thus possible, with relatively moderate currents, to fuse a thin platinum wire which may be interposed in the circuit. The luminous effects of voltaic electricity are obtained under two distinct conditions: First, when two wires from the electrodes of a battery are brought together, thus closing the circuit, a spark is seen at the point of contact, often of great brilliancy. This is also seen on breaking the circuit. Secondly, the resistance offered to the passage of the current through a poor conductor often heats the latter to such a degree that it becomes luminous. Both of these methods of obtaining luminous effects, we will see later (see p. 146), are practically applied in electric lighting.

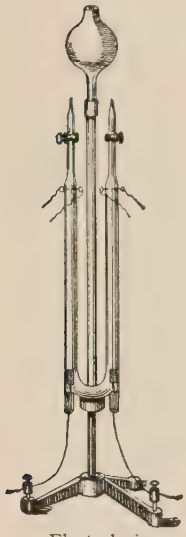
The chemical effects of the battery current are notably more important than are those of frictional electricity, because the greater amount of electricity and the duration of the current in the first case make possible effects not to be attained in the other case. Thus the current passed through acidified water, as shown in Fig. 72, will decompose it into its constituents, hydrogen and

oxygen gases, by a process termed *electrolysis*. Similar results are obtained with solutions of many chemical salts. This will be more fully treated of later under the electro-deposition of the metals, or electro-metallurgy (see p. 863).

Electro-Magnetics.

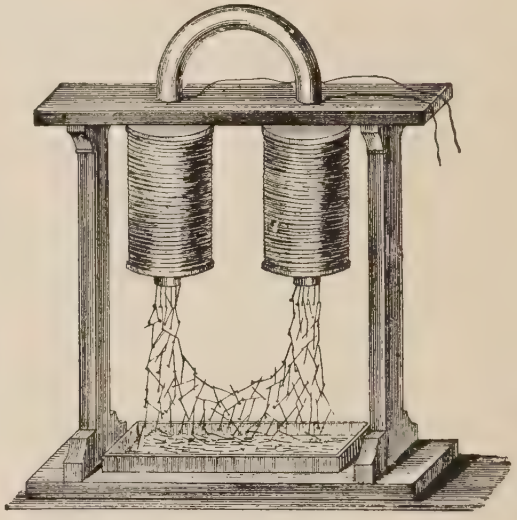
9. The Electro-Magnet.—The magnetic effects of the voltaic current are so important that they require special consideration. If a bar of soft iron is held at right angles to a wire carrying a current of electricity, we will find that it acquires for the time being magnetic properties. If the wire be coiled around the bar, the magnetic effect will be increased in proportion to the number of coils. To make a powerful horseshoe magnet, therefore, it is only necessary to take two short bars of soft iron joined at one end by a cross-piece of similar metal, surround these bars

Fig. 72.



Electrolysis.

Fig. 73.



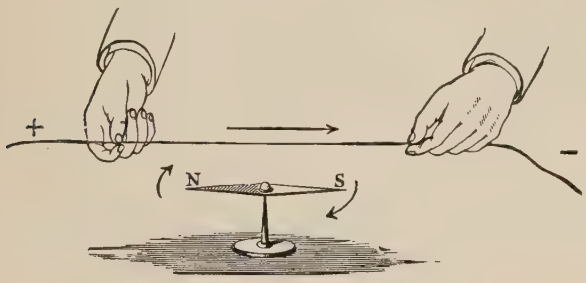
Electro-magnet.

by coils or bobbins of insulated wire, and pass a current through the coils. While the current passes we have, as shown in Fig. 73, a powerful magnet, but, as soft iron has little or no coercive force, the moment the current ceases the magnetism of the iron cores disappears. The coils should be wound or connected so that the current passes around one coil in one direction and around the other in the opposite direction, in order that one

shall form a north pole and the other a south pole. Electro-magnets are used in almost all forms of practical electrical apparatus.

The Galvanometer.—In 1819 Oersted made the discovery that a magnetic needle tends to set itself at right angles to a wire which carries an electric current, and that this deflection is

FIG. 74.



Influence of current on compass.

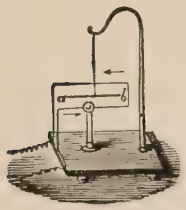
governed by the direction of the current. For example, if an insulated copper wire attached to both poles of a battery is held above and parallel to a magnetic needle, and the current flows along from north to south, it will cause the north end of the needle to turn eastward (Fig. 74); if the current flows from the south to the north in the wire, the north end of the needle will be deflected westward. If the wire is held below the needle, the movements of the needle will be reversed,—that is, the current flowing from north to south will cause the north pole of the magnet to turn westward.*

If instead of using a straight wire it is bent in the form of a loop so that the current will pass above and below the needle (Fig. 75), the deflecting force of the current will be doubled, for the current flows above and below in opposite directions; hence both deflect the needle in the same direction. Such an arrangement is called a *galvanoscope*, and serves in a rough way to indicate the presence and direction of currents (see Ampère's rule). To render this instrument more sensitive and adapt it for quantitative use, the number of turns of wire

* In order to retain these movements we cite the rule of Ampère,—namely, *the observer imagines a small human figure swimming with the current, its face being constantly towards the needle and its arms extended. The* **left** *hand will indicate the direction of the north pole's deflection.*

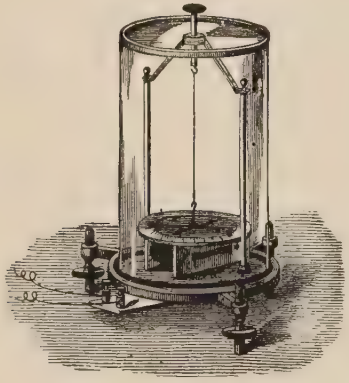
around the needle must be increased, and the directive force of the earth's magnetism, which tends to keep the needle pointed north and south, must be decreased by some compensating arrangement. This usually consists in placing a magnetic needle above, with its poles reversed to the one in the coil below; such a contrivance is known as an *astatic combination* (Fig. 76), and the instrument as a *galvanometer.** A galvanometer is an instrument used for measuring the strength of electric currents by means of their electro-magnetic action, and according to their construction they may be divided into two general classes: (*a*) those in which the current flows in a fixed coil of wire, causing the deflection of a pivoted or suspended magnetic needle (Fig. 76); (*b*) those in which the current flows in a movable coil suspended between the poles of a fixed magnet, causing the coil to turn.

FIG. 75.



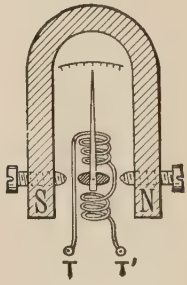
Galvanoscope.

FIG. 76.



Galvanometer.

FIG. 77.



Ammeter.

Voltameters and Ammeters.—If a galvanometer be made with a very long thin wire coil of high resistance, very little current will flow through it; however, what current does flow will be

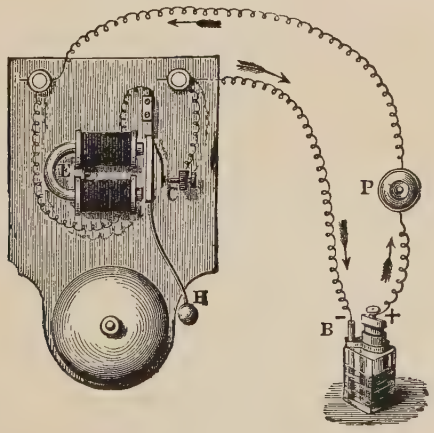
* A galvanometer for measuring very minute currents must have many windings of fine wire, for the current must circulate hundreds or thousands of times around the needle in order to multiply its effects so as to turn the needle; this must also be the case if the current has passed through a long circuit or one of high resistance, as, for example, the telegraph. Large currents need a coil of thick wire of but few turns.

exactly proportional to the potential difference between the two poles of the circuit; hence will indicate pressure or voltage of the current. Such an instrument is called a *voltameter*, or potential galvanometer, of which there are several forms; but all are alike in that a coil of high resistance (sometimes several thousand ohms) is employed. The *ammeter* (*ampère-meter*) is a galvanometer the coils of which consist of but a few turns of low resistance wire, for $C = \frac{E}{R}$. Other forms of voltameters and ammeters (Fig. 77), based on class *b*, consist of an armature of soft iron, around which are wound the coils of insulated wire. This is then suspended between the poles of a powerful horse-shoe magnet. Attached to this armature core is a needle indicator, whose deflections indicate the strength of the current. The magnet controls the direction of the armature with its needle, and makes it independent of the earth's magnetism. Still other instruments depend on the magnetizing influence of the current on strips of iron, whereby one, attached to an indicator, is attracted or repelled by the other.

Applications of Electro-Magnetism.

10. Electric Bells.—These are based on the principle of the electro-magnet, which, by attracting and releasing an armature,

Fig. 78.



Electric-bell system.

to which is attached a hammer, causes a backward and forward movement, striking a bell. The working of these is shown in

Fig. 78, in which the electro-magnet, E, is controlled by a Leclanché or dry cell. The instant that the circuit is closed by pressing the button, P (Fig. 78), the current flows through the coils and causes the electro-magnet to attract the armature with hammer, H. This forward movement of the armature breaks the circuit, for the current passes through it and the spring contact-breaker resting against the tip of the screw, C, from whence it passes back to the zinc pole of the battery. The circuit having been broken, the electro-magnet ceases to attract, but the momentum already imparted carries the hammer forward. Immediately afterwards, however, the spring forces it back to its original position. These movements are repeated in rapid succession as long as the circuit is kept closed.

11. **Electric Clocks.**—By means of a standard central clock, which is in electric connection with a circuit containing any number of dials, the circuit is made and broken periodically by the oscillations of its pendulum. These transmitted currents attract an armature behind each dial on the circuit, which controls the movement of a ratchet wheel, permitting it to move forward through one tooth at the specified interval, so that the hands of all the clocks move simultaneously with those of the standard clock.

12. **Telegraphy.**—The telegraph cannot be assigned to any particular inventor, for it has passed through successive stages to its present state of perfection. Lesage (Geneva, 1774) was the first to construct a telegraph, in which 24 wires were employed, each wire being connected with a pith-ball electroscope representing a letter of the alphabet. Joemmering (Munich, 1808) employed 35 eudiometer tubes, each separately connected, and the electrolytic decomposition of the water contained in each served as a signal. Weber and Gauss (Goettingen, 1833) employed the right and left deflections of a galvanometer needle to indicate a code of signals. Steinheil (Munich, 1837) discovered that the current could be carried by a single wire, the earth being used in place of a return wire. Henry (New York, 1831) utilized the attraction of an electro-magnet on an armature to produce sound signals, and Morse (1835) devised a code of alphabetic signals, consisting of dots and dashes, which were made on moving strips of paper. The telegraphic apparatus consists of

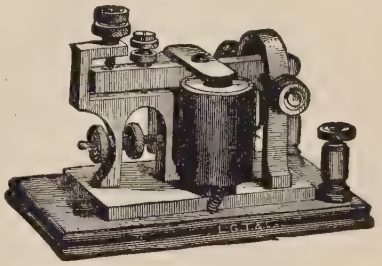
1. *The Battery and the Wire Circuit.*—The kind of battery employed varies in different countries, but is usually some modi-

fication of the Daniell cell. A galvanized iron wire connects the different stations, while the return current is provided for by ground plates sunk in the earth, which acts as a common reservoir, giving and receiving electric energy rather than conducting it.

2. *The Communicator, or Key.*—This consists of a horizontal lever, by means of which the sender controls the current and can establish or break contact by pressure of the finger, producing at the receiving station the clicks or signals.

3. *The Sounder* (Fig. 79) is the receiving instrument, which is an electro-magnet. This, when the current passes through the coils, attracts an armature for a longer or shorter period of time. This instrument can be arranged as a "sounder," in which the movements of the armature cause a clicking sound by striking against a stop; or as a "register," in which case the armature, by means of an attached pin, prints dots and dashes upon a strip of paper drawn through the instrument by means of clock-work. The Morse system, which is universally employed, uses as alphabet a series of dots and dashes, indicated by longer or shorter clicks, as heard from the sounder or imprinted on paper.

FIG. 79.



Telegraphic receiver (sounder).

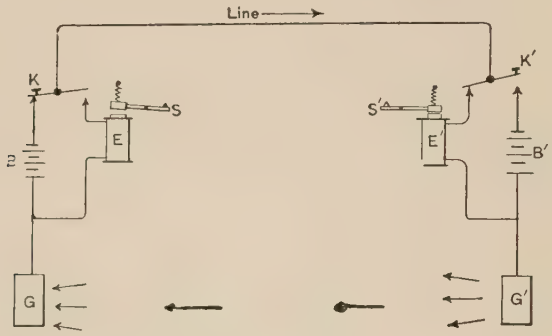
4. *The Relay.*—On lines of not over thirty miles in length the sounders can be operated by the current generated by the batteries of the terminal stations, but on longer lines the resistance weakens the current to such an extent that a relay, or repeater, which consists of an additional electro-magnet with a local battery, must be inserted.

Fig. 80 illustrates the simplest possible case of an open single-current circuit method of telegraphing. On depressing the key, K, the current flows from the battery, B, through the line and enters the receiving instrument, causing the electro-magnet, E′, to attract the sounder, S S′, returning through the ground plate, G′, to G and the battery whence it started. If key, K′, is depressed, the reverse action takes place.

Duplex, Diplex, and Quadruplex Telegraphy.—Two messages sent through the same wire simultaneously, from opposite termi-

nals, constitute "duplex" telegraphy; when both are transmitted through the same wire in the same direction, "diplex;" while "quadruplex" telegraphy combines both the duplex and the diplex systems.*

FIG. 80.



Principle of telegraph.

Cable or Submarine Telegraphy.—The transmitting cable is made of seven or more No. 16 copper wires, protected, first, by a layer of gutta-percha, then by a woven coating of jute. Outside of this is a layer of at least ten steel wires, which are still further protected by wrapping in hemp. Strong currents cannot be employed, for the cable and its non-conducting sheath, when immersed in water, produce excessive electrostatic charges, like those of the Leyden jar, which impede electric transmissions. For each signal a current is sent into the cable, followed by a reactive opposing current, which again discharges it. Since the currents transmitted are very weak, it is necessary that an exceedingly sensitive receiving apparatus be employed. This is a galvanometer, called Lord Kelvin's Siphon Recorder, which consists of a coil of wire suspended between the poles of a powerful magnet. To this coil is attached a fine glass siphon, one extremity of which dips into a vessel of ink, and as the coil oscillates backward and forward like the needle of an ordinary galvanometer the ink flows from the siphon, producing on a moving strip of paper a wavy line, having short and long waves for dots and dashes. The duplex system is used on all cables. The rate of speed for messages varies according to the length of the cable; the fast cable between

* For explanation of these systems, see Electricity and Magnetism, by S. P. Thompson, published by the Macmillan Company.

Newfoundland and Ireland admits 100 letters (about 25 words) per minute, the speed decreasing with the distance.

Wireless telegraphy is based on the transmission of electric waves through space. The distance through which we may communicate is limited, owing to the reflection of the waves by the earth's curvature. However, by employing very tall transmitting and receiving wires, the distance may be increased accordingly. Messages have thus been transmitted across the English Channel. The transmitting instrument is a vertical wire pole from 50 to 100 feet high ; with it is connected one of the knobs of an induction coil, while the other knob communicates with the ground. Every spark which passes between the knobs at the bottom of the pole answers as a signal dot, while a short succession of sparks indicates a dash. These sparks produce electric pulsations in the vertical wire, which are communicated as waves in every direction through space. As receiver, a like wire is employed, to which is attached a specially constructed but simple apparatus called a "coherer." This is a glass tube fitted at both ends with rubber stoppers, and through these pass the two electrodes of a battery, the tips of which terminate in metallic disks. Between these two disk terminals, which are some distance apart, is a layer of coarse iron, nickel, or silver filings ; these offer a very high resistance to the passage of the current. Attached in this same circuit is an electro-magnet receiver. The instant the transmitted electric waves fall on the vertical wire connected with this coherer its resistance is reduced, and a current flows through the circuit and operates the electro-magnet of the receiver, producing dots and dashes of the Morse code.

Voltaic Induction.

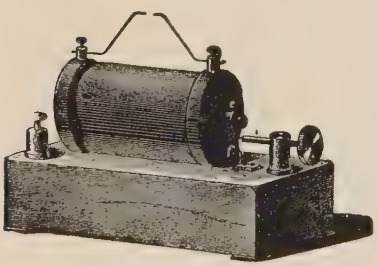
13. Induction Currents.—Faraday (1831) made the discovery that instantaneous currents of electricity are produced in closed circuits by the movement of a magnet in proximity to them ; also by a similar movement of a conductor traversed by an electric current ; a current whose strength is changing will produce the same effect. Such currents are known as faradic or induced currents, and on this principle are based the induction coil, dynamo machines, alternate current transformers, etc.

(*a*) *Induction of Currents by Currents.*—To illustrate this two coils of insulated wire, wound on spools, are selected. One of these, known as the *primary* or *inducing current* coil, is made

sufficiently small to fit inside of the other, and its terminals are connected with a battery. The terminals of the larger coil, which is called the *secondary* or *induced current* coil, are connected with a galvanometer. If the primary (smaller) coil is introduced inside of the secondary (larger), the galvanometer will show that a reverse current of momentary duration has been induced in the latter, moving in the opposite direction to that circulating in the primary. The instant the primary current ceases to flow or the coil is withdrawn, a direct current is induced in the secondary coil, moving in the same direction as that of the primary.

(*b*) *Induction of Currents by Magnets.*—If in the above experiment the primary coil is substituted by a magnet, it will be found that on inserting a bar magnet inside of the secondary coil the needle of the galvanometer will be deflected, showing thereby that an electric current has been induced. This current is of momentary duration only, and when the magnet is withdrawn the needle will be deflected in the opposite direction, showing the induction of a reverse current. If the poles of the magnet be reversed the direction of each current will be reversed. This subject will be further explained under magneto-electric currents, p. 143.

FIG. 81.



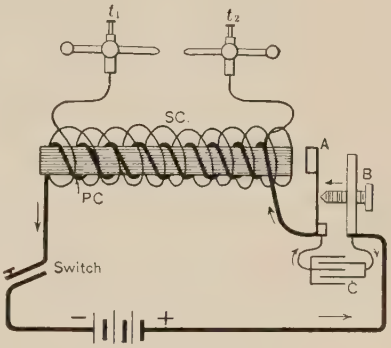
Induction coil.

The Induction or *Ruhmkorff Coil* is a practical application of the preceding principles. By means of this we are able, with a few voltaic cells, to produce an exceedingly high E.M.F. or potential difference, which in a large coil is equivalent to many thousand volts. For example, a battery of 600,000 Daniell cells would be required to produce a spark of 6 inches, while, by aid of an induction coil, the same may be accomplished with perhaps 10 cells. An induction coil (Figs. 81, 82) consists of a central core made of a bundle of soft iron wires*

* A bundle of soft iron wires is employed as electro-magnet in preference to one of solid iron, because of the rapidity with which the wires can be magnetized and demagnetized; the latter always retains (after cessation of the current) a small amount of residual magnetism which would interfere with the rapid making and breaking of the current.

around which is wound a few turns of heavy insulated copper wire (P C, Fig. 82) of low resistance, in order that it may carry strong magnetizing currents. The one terminal of this coil connects with a switch and this with the negative pole of a battery, the other is attached to the spring of the *vibrator* or *contact breaker*, A, resting against the set-screw, B, which communicates with the positive pole of the battery. This is called the *primary circuit.*

FIG. 82.



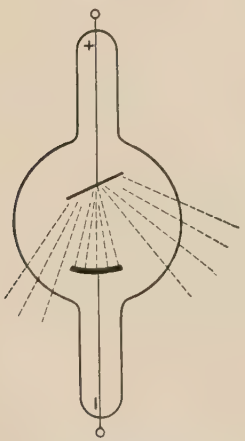
Outlined induction coil.

On closing the circuit (by means of the switch) the electro-magnet core of the primary coil attracts the vibrator, A, which, the instant it leaves the set-screw, B, breaks the circuit. The core loses thereby its magnetism, and the vibrator is forced back to its original position by its spring, which again closes the circuit, as before. The make and break thus produced take place with great rapidity, giving rise to a series of *primary intermittent* currents. By means of the set-screw, B, the amplitude of the vibrations may be regulated. Around the primary coil, and insulated from it by means of a hard-rubber casing, is the *secondary circuit*, S C, which consists of many turns of the thinnest wire. For example, a giant coil which gives a spark of about 1 meter contains 480 kilometers (300 miles) of wire in its secondary circuit, with a resistance of over 100,000 ohms. The terminals of this coil end in the knobs, t^1 and t^2, across the points of which, when adjusted to the proper distance, brilliant, snappy sparks will pass. Every "make" of the intermittent current in the primary circuit results in the induction of a momentary *inverse* current in the outer secondary circuit, and at every "break" a powerful momentary *direct* current ; thus *alternating intermittent secondary currents* of high potential follow in rapid succession. Connected with the primary circuit is a condenser, C, made of alternate layers of tin-foil and paraffine paper, into which the extra current flows when the circuit is broken, thereby increasing the E.M.F. at the "break." Small induction coils are employed in treating nervous diseases ; also for electric gas-

lighting, exploding mines, and bringing about chemical union between gases.

The passage of a spark * between the terminals t^1 and t^2 is accompanied by a loud snapping noise, which is due to the resistance offered by the air ; if, however, this discharge is made to take place between two platinum electrodes sealed in the extremities of glass tubes which have been rarefied to the extent of $\frac{3}{1000}$ part of an atmosphere, a beautiful luminous phenomenon is produced, the color and appearance varying with the degree of exhaustion, diameter of the tube, and nature of the rarefied gas remaining. Such tubes are known as *Geissler tubes*, and, besides being rarefied, they are often made of fluorescent (uranium) glass or the outer walls filled with fluorescent liquids. If the exhaustion of such tubes be carried to a very high degree, so that only about $\frac{1}{1000000}$ part of the air originally contained remains, we will find, on connecting with the terminals of a 5- to 6-inch coil, that no electric discharge as heretofore seen takes place ; but a purplish ray is seen about the cathode, while the interior of the tube remains dark and the glass walls become greenish fluorescent. It was found that the discharge from only one of the electrodes—namely, the cathode (— pole), irrespective of the position of the anode (+ pole)—was capable of producing this fluorescence of the glass walls of the tube, and that when directed on powdered alumina, rubies, and diamonds it caused them to become phosphorescent. Tubes specially constructed for this purpose are known as *Crookes tubes* (Fig. 83).

Fig. 83.



Crookes tube, showing reflection of "X-rays."

To Professor Roentgen is due the credit of the discovery that this cathodic discharge (called by him "X-rays") is capable of penetrating opaque bodies and exciting certain fluorescent substances. Of these, the two best adapted are platino-cyanide of barium and calcium tungstate. If a piece of pasteboard is covered with a layer of either of these chemicals,† and is held

* This differs only in degree from that furnished by the frictional machine or Leyden jar.

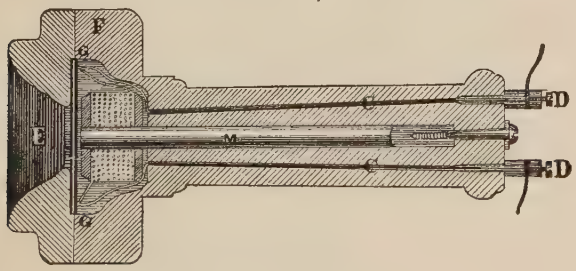
† Such a screen was named by Edison the Fluoroscope.

so that the "X-rays" are directed upon the screen, its surface will become uniformly illuminated. If now any opaque or semi-opaque object is placed between it and the Crookes tube, the rays will either be uniformly intercepted or some more intercepted than others; hence shadows will result. For example, the bones of the hand intercept the rays more than the fleshy parts; hence cast shadows whereby they may be distinguished. The cathode is usually cup-shaped, in order to focus the rays upon a flat, disk-shaped anode, which acts as a reflector.

While glass is relatively opaque, wood, paper, and most organic tissues are transparent, and allow the passage of these rays. They act upon the photographic plate, and admit photographs being taken through wood and most organic tissues. The metals, with the exception of aluminum, are more or less opaque to them.

The telephone is a much more practical application of the principles of induction. By its means speech may be transmitted through long distances by the intervention of a magnet and induced currents in a coil of wire surrounding the magnet. The essential parts of the Bell telephone can be seen in Fig. 84. Enclosed in the case, F, is a magnet, M, having at one end a coil of very fine wire, and a diaphragm of very thin sheet-iron, GG, which is placed close in front of the magnet. The coil of wire connects by the two wires CC with binding screws, DD, at the other end of the instrument. When a person speaks into the mouthpiece, E, the diaphragm of thin metal vibrates immediately before

FIG. 84.



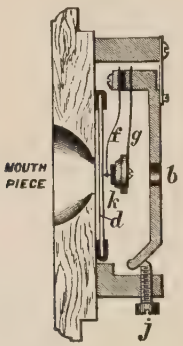
Telephone.

the magnet and causes changes in the lines of magnetic force and so electric currents in the coil which surrounds it. These currents passing over the line affect the strength of the magnet in a corresponding instrument at the other end, and in turn cause the

diaphragm in front of it to vibrate, producing sound waves which will perfectly correspond with those generated by the person speaking. The Bell telephone may therefore serve either as a "receiver" or a "transmitter."

In modern telephones the Blake transmitter (Fig. 85) is em-

Fig. 85.



Blake transmitter.

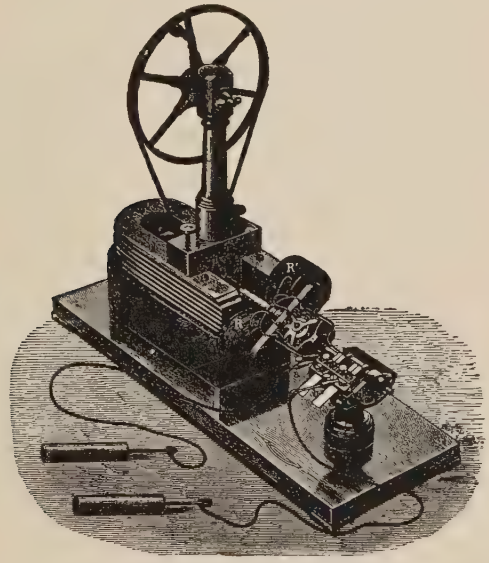
ployed. In this the voice-vibrations directed into the mouth-piece fall upon the thin iron diaphragm, *d*, which is held in place by a soft-rubber ring. The vibrations of this are transmitted by the insulated spring-needle, *f*, to a carbon plug, *k*, attached to a spring, and the current passes to the contact point by one spring and passes off through the other.

CHAPTER VIII.

MAGNETO-ELECTRIC AND DYNAMO-ELECTRIC GENERATORS.

By means of machines we are able to convert mechanical energy into electrical energy. This involves an expenditure of force in producing relative motion between magnets and conductors, which consists, in most instances, in rotating coils of

Fig. 86.



Magneto-electric machine.

wire in the field of a magnet or electro-magnet, or in other cases the latter are made to revolve.

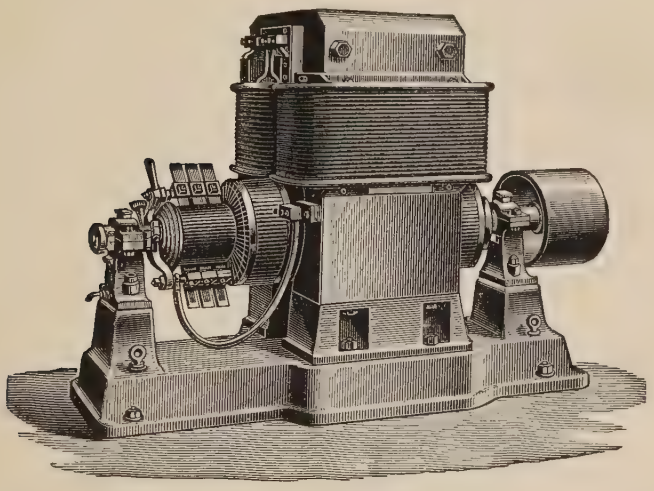
Simple Magneto-Electric Machine.—The discovery of Faraday, that if a coil of wire is moved across the field of a magnet electric currents are induced (see p. 137), first suggested the construction of the magneto-electric machine, whereby electric currents could be generated by mechanical power. Such a

machine is shown in Fig. 86. In front of a powerful horseshoe magnet, and as near as possible, rotates an armature consisting of two soft iron cores, R, R′, each of which has been wound with a coil of insulated copper wire ; the ends of the wires connect with the axis, and from this, by means of two springs, the currents are taken up and carried to the handles from *a b*. When the armature revolves, the soft iron cores, as they pass in front of the north and south poles of the magnet, become magnetic by induction ; this induces in each of the coils transient currents which are alternately inverse and direct. Since the poles change twice in every revolution, the direction of the current will necessarily change twice. In order that the currents may all flow in the same direction, as in the galvanic battery, a *commutator* is fixed on the axis ; this consists of two semi-cylindrical segments of copper, each insulated from the axis and connected with the ends of the separate coils. When rotating, these two plates are out of contact with the springs during the break, and are brought into reversed contact at the instant of current reversal, which occurs at each half revolution. Their position with reference to the springs is reversed as the currents are reversed ; hence the latter flow in the same direction. Thus, by means of a commutator, direct currents can be made up from alternating ones, with, however, a perceptible intermission at each make and break ; this lessens with the rapidity of rotation.

The Dynamo-Electric Machine.—This machine (Fig. 87) differs from the preceding in that the permanent magnet is replaced by an electro-magnet, which is excited by the current generated. In proportion as the strength of the current circulating around the electro-magnet increases, the magnetic forces multiply, which in turn induce still stronger currents in the coils which rotate within the field of influence. The number of magnetic poles is frequently increased from two to four and even eight ; such are known as multipolar dynamos. Between the poles, or field magnets, of the dynamo rotates an armature of soft iron, made either in the form of a ring, over which the insulated coils of wire are wound, known as the *Grammes ring*, or the armature and its coil are drum-shaped, and called the *Siemens armature*. The ends of the armature coils all terminate in a number of copper strips attached to the axis, but insulated from one another, and from these the current is taken up by two sets of brushes, which consist of a number

of copper bars set close to the commutators. If the transient currents generated by the rotating armature pass into the external circuit without commutation, a continuous *alternating* current is produced, and machines having such a construction

FIG. 87.



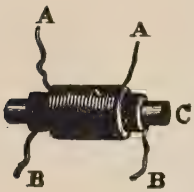
Dynamo-electric machine.

are called alternating-current dynamos. The advantages of this kind of a dynamo, with its currents, are several: for example, the resistance and wasteful sparking of the split ring commutator are avoided; it gives currents of higher potential and less internal resistance than the direct-current dynamo; also, it is possible to carry such currents to distances with comparatively small wires and at less cost. A *motor* is a machine which is utilized in converting electrical energy into mechanical; the dynamo, as shown in Fig. 87, can be used as a motor if supplied with a proper current.

Transformers or *Converters* are necessary in the distribution of alternate currents. Their function is to transform currents of high pressure and low quantity into induced currents of low pressure and larger quantity. For instance, a high-pressure current of from 1000 to 5000 volts flowing through the mains must be cut down to 50 or 100 volts for incandescent lighting in the various branches. These transformers (Fig. 88) are simply inverted induction coils, in which the primary coil consists of

many turns of fine wire, which receives a small current of high pressure from the mains. Insulated from this is the secondary coil of a few turns of coarse wire of low resistance, which gives out a large current of low pressure. If the primary coil has 2000 turns and the secondary 100 turns (ratio of 20 to 1), in order to take out of the latter a current of 100 ampères and 50 volts, we must put into the primary coil (from the main) at least 5 ampères at 1000 volts' pressure. By selecting the proper number of turns, the E.M.F. can be transformed up or down.

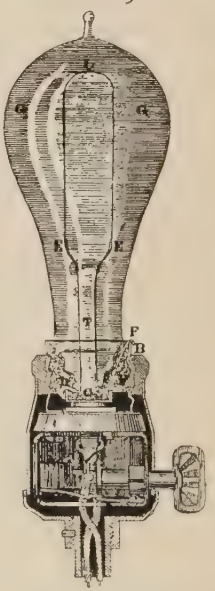
FIG. 88.



Transformer.

Change of Electrical Energy into Heat.—We have already referred to the heating effect of the voltaic current. The heat generated by the powerful currents of the dynamo machine, when passing through poor conductors or encountering electrical resistance in any way, is correspondingly greater. Two effects of this heating may be noticed: *electrical furnaces* for carrying out metallurgical operations which require an intense heat, as in the Cowles furnace for the production of aluminum by the reduction of its oxide by charcoal; and *electric welding*, in which case two pieces of metal are welded together by bringing them in contact and passing a powerful electric current through the juncture. Iron, steel, brass, and copper may be welded in this way with great success.

FIG. 89.



Edison incandescent lamp.

Change of Electrical Energy into Light.—The heating effect of powerful currents may be utilized for lighting purposes in one of two ways. If the two electrodes of the current from a powerful battery or dynamo be brought to within a short distance of each other, a brilliant arc light is formed, spanning the interval between the two terminals. The ends of the wires are raised to a white heat, and most metals melt or volatilize in consequence. If, however, the terminals are pencils of hard carbon, which is infusible, we have the brilliant white light known as the *arc light*.

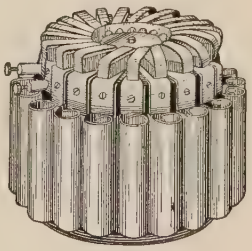
The carbon, of course, burns away gradually, and provision must be made for keeping the distance between the two pencils constant, which is done automatically by a suitable mechanism attached to the lamp.

The current is also utilized for lighting effects in a still simpler way. This is to interpose at some point in the circuit a conductor of such resisting power that the passage of the current renders it white-hot. This is effected in the *incandescent lamp*, and the substance utilized here is likewise carbon. An extremely fine filament of carbon is enclosed in an exhausted glass globe, as shown in Fig. 89, which illustrates the Edison lamp. This filament or horseshoe of carbonized bamboo is connected at either end by fine platinum wires, which are fused into the glass and pass through, connecting with the brass fitting of the socket into which the lamp is screwed.

Arc lamps require a very high electro-motive force, usually from 1000 to 3000 volts. Incandescent lamps, on the other hand, require only from 50 to 120 volts. The one current is likely to be fatal to life if by accident a naked wire is touched, the other is not.

Thermo-Electric Currents.—If two dissimilar metals are soldered together, and either heated or cooled at their point of contact, an electric current is produced; such currents are termed *thermo-electric currents*. The two bars of metal producing the current constitute the *thermo-element*. A number of such elements or metal bars thus joined and arranged side by side in couples, with each pair of ends soldered together in alternate order, form a *thermopile*, one form of which is shown in Fig. 90. For various reasons, very few metals are available for this purpose. Those combinations usually employed consist of either bismuth and antimony or German silver with an alloy of antimony and zinc. Thermo-currents are of extremely low potential and very constant. The thermopile, when connected with a sensitive galvanometer, affords accurate means for detecting very minute differences of temperature, but has no other practical application.

FIG. 90.



Thermopile.

PART II.

CHEMISTRY OF THE NON-METALS.

CHAPTER I.

THEORETICAL INTRODUCTION.

Matter is that which occupies space and is apprehended by the aid of our senses. Close observation teaches us that matter is constantly subject to changes, and these may be of two distinctive characters,—namely, *physical* and *chemical.*

Physical Changes.—These are changes of condition without alteration of the identity of matter : for example, when water is heated it is converted into vapor or steam ; this, on cooling, condenses to water. If we cool water sufficiently it crystallizes, —that is, it is converted into ice. Such changes affect only the outward or physical appearances of the water.

Again, on bringing a piece of iron in contact with loadstone it acquires the property of attracting and holding to itself other pieces of iron,—that is, it becomes magnetic. This same iron may be heated until it gives off light and heat, yet these changes which the iron has undergone are all of a purely physical character ; it has not lost its identity as metallic iron.

Chemical Changes.—In changes of this character the substance loses its individual properties, and something else is formed in its place which possesses entirely new properties. The substance has lost its identity. For example, if we allow the electric current to act upon water it rapidly loses its identity as water in being resolved into two different invisible gases,— namely, hydrogen and oxygen. These products no longer possess any characteristics in common with water.

Again, on exposing iron to moist air it soon begins to rust, and if this is allowed to continue sufficiently long, the iron completely disappears, leaving in its stead a deposit of reddish-brown powder, which is infusible and no longer attracted by the magnet. If iron be brought in contact with a liquid known as hydrochloric (muriatic) acid it rapidly disappears, having been

dissolved by this acid, with the production of a new compound. In these two changes just cited we observe that the iron has lost its identity as such,—that is, it no longer possesses the characteristics of iron as a metal; it has undergone chemical changes.

Mechanical Mixtures and Chemical Compounds.—If we mix iron filings and sulphur, a gray-colored powder is obtained. This represents a mechanical mixture, so called because the two ingredients can be separated by mechanical means. By the use of a magnet the iron filings may be removed from the sulphur, or the latter may be taken up by means of a solvent, leaving the filings behind.

If this mechanical mixture be heated by the direct application of a flame, the entire mass will soon begin to glow, and after cooling a black fused mass remains which no longer resembles either iron or sulphur. Examination with a lens will no longer reveal any particles of either iron or sulphur, nor will the magnet or treatment with a solvent remove either one of the ingredients. These have lost their identity with the formation of a chemical compound known as iron sulphide. Gunpowder is a mechanical mixture of sulphur, saltpetre, and charcoal. By means of the solvent carbon disulphide the sulphur may be removed, while subsequent washing with water eliminates the saltpetre, leaving the charcoal behind. If this mixture be ignited, a flash with explosion results, which is due to the sudden chemical combination which takes place among the ingredients of the mixture.

From this we learn that when substances undergo chemical changes they lose their individual characteristics, which have merged into the new compounds formed. Accompanying these chemical changes may be evolution of heat, or heat and light, changes in aggregate condition, as liquid to solid or gaseous, or *vice versa.*

In the combination of the iron with the sulphur, or the explosion of the gunpowder, we effect chemical changes which result in the production of new substances of essentially different properties. Such changes have been brought about by a form of energy called chemical affinity.

Chemical affinity is the attractive force which causes different elements to unite, resulting in the formation of new substances of different properties. This same attractive force causes atoms to unite, forming molecules. All elements possess this affinity in a greater or less degree, some combining with great force,

as in the explosion of gunpowder, while others may be caused to combine with some difficulty, and still others do not unite at all. The degree or intensity of affinity varies frequently in the same element. The various conditions necessary to bring about chemical combination—a result of this attractive force—will be taken up on p. 165.

Kinds of Chemical Changes.—The various chemical changes thus far cited are more properly known as *reactions.* These may be divided into two classes,—namely, synthetic and analytic.

Synthetic reactions are those in which various substances unite with the production of new compounds of different properties. As, for example, the combination of sulphur and iron to iron sulphide, or when an electric spark is passed through a mixture of hydrogen and oxygen gases they unite to form water.

Analytic reactions are those in which we resolve a chemical compound into its various constituents: the reverse of synthetic reactions. For example, by the action of the electric current upon water it is resolved (decomposed) into the invisible gases oxygen and hydrogen. If red precipitate, a compound of mercury and oxygen, be heated, the latter (a gas) is liberated, leaving mercury behind. These analytic reactions may all be verified by synthetic reactions, whereby the products of the former are again caused to unite.

Chemistry is the science which treats of the composition of matter, together with the study of the phenomena under which alterations through the influence of chemical force take place.

Nature of Matter.—Chemists consider that matter (solid, liquid, or gaseous) is made up of exceedingly small discrete particles called molecules (*molecula* = a minute mass), which possess the distinctive properties of the masses from which they are obtained. *A molecule is the smallest particle of matter into which substances can be divided without losing their identity.** When we arrive at our physical limit of subdivision, we still find that each molecule is capable of *chemical* subdivision,—that is, each ultimate particle is made up of elementary substances called atoms (a, $\tau\epsilon\mu\nu\omega$ = indivisible), these being the indivisible constituents of molecules.

An atom is the smallest particle of simple matter which can

* It has been estimated that if a drop of water be expanded (without additions) to the size of the earth, its molecule would be about the size of a bird shot.

enter into the composition of a molecule. Atoms are incapable of existing in the free state; hence when liberated by chemical action they unite at once to form molecules. Most elemental molecules consist of two atoms; as exceptions, ozone (a form of oxygen) contains three, while phosphorus and arsenic each contains four.

Elements.—By applying various methods of analysis to the different forms of matter found in nature, chemists have isolated over seventy elements. *An element is a substance which cannot by any means known to chemists be resolved into anything else essentially different from itself.* Thus, chemists have been unable to resolve oxygen gas into anything simpler, nor can sulphur be made to yield any other kind of matter; hence these are termed elements.

TABLE OF ELEMENTS.

Element.	Symbol.	Atomic Weight. H = 1	Atomic Weight. O = 16
Aluminum	Al	26.9	27.1
Antimony (*Stibium*)	Sb	119.5	120.4
Argon	Ar	?	?
Arsenic	As	74.45	75.0
Barium	Ba	136.4	137.40
Bismuth	Bi	206.5	208.1
Boron	B	10.9	11.0
Bromine	Br	79.34	79.95
Cadmium	Cd	111.55	112.4
Cæsium	Cs	131.9	132.9
Calcium	Ca	39.8	40.1
Carbon	C	11.9	12.0
Cerium	Ce	138.0	139.0
Chlorine	Cl	35.18	35.45
Chromium	Cr	51.7	52.1
Cobalt	Co	58.55	59.00
Columbium	Cb	93.0	93.7
Copper (*Cuprum*)	Cu	63.1	63.6
Erbium	Er	164.7	166.0
Fluorine	F	18.9	19.05
Gadolinium	Gd	155.8	157.0
Gallium	Ga	69.5	70.0
Germanium	Ge	71.9	72.5
Glucinum	Gl	9.0	9.1
Gold (*Aurum*)	Au	195.7	197.2
Helium	He	?	?
Hydrogen	H	1.000	1.008
Indium	In	113.1	114.0
Iodine	I	125.89	126.85
Iridium	Ir	191.7	193.1
Iron (*Ferrum*)	Fe	55.6	56.0
Lanthanum	La	137.6	138.6
Lead (*Plumbum*)	Pb	205.36	206.92
Lithium	Li	6.97	7.03
Magnesium	Mg	24.1	24.3
Manganese	Mn	54.6	55.0
Mercury (*Hydrargyrum*)	Hg	198.50	200.0
Molybdenum	Mo	95.3	96.0
Neodymium	Nd	142.5	143.6
Nickel	Ni	58.25	58.70
Nitrogen	N	13.93	14.04
Osmium	Os	189.6	191.0
Oxygen	O	15.88	16.000
Palladium	Pd	106.2	107.0
Phosphorus	P	30.75	31.0
Platinum	Pt	193.4	194.9
Potassium (*Kalium*)	K	38.82	39.11
Praseodymium	Pr	139.4	140.5
Rhodium	Rh	102.2	103.0
Rubidium	Rb	84.75	85.4
Ruthenium	Ru	100.9	101.7
Samarium	Sm	149.2	150.3
Scandium	Sc	43.8	44.1
Selenium	Se	78.6	79.2
Silicon	Si	28.2	28.4
Silver (*Argentum*)	Ag	107.11	107.92
Sodium (*Natrium*)	Na	22.88	23.05

Element.	Symbol.	Atomic Weight. H = 1	Atomic Weight. O = 16	Element.	Symbol.	Atomic Weight. H = 1	Atomic Weight. O = 16
Strontium	Sr	86.95	87.60	Titanium	Ti	47.8	48.15
Sulphur	S	31.83	32.07	Tungsten (*Wolfram*)	W	182.6	184.
Tantalum	Ta	181.5	182.8	Uranium	U	237.8	239.6
Tellurium	Te	126.5	127.5 ?	Vanadium	V	51.0	51.4
Terbium	Tb	158.8	160.	Ytterbium	Yb	171.9	173.2
Thallium	Tl	202.61	204.15	Yttrium	Yt	88.3	89.0
Thorium	Th	230.8	232.6	Zinc	Zn	64.9	65.4
Thulium	Tu	169.4	170.7	Zirconium	Zr	89.7	90.4
Tin (*Stannum*)	Sn	118.1	119.0				

Names of the Elements.—The names of the elements are usually derived from some distinguishing feature or peculiarity. Thus, *chlorine* (from χλωρός = *yellowish green*) refers to the characteristic color of the gas; *hydrogen* (compounded from ὑδωρ = *water* and γεννάω = *I produce*) derives its title from the fact that it is a necessary constituent in the production of water; the title *argon* (from αργος = *no energy*) refers to its chemical inertness; such elements as *gallium*, *germanium*, and *scandium* have derived their titles from the old Latin names referring to the nationality of the discoverer.

Symbols of the Elements.—In expressing the composition of different chemical substances which are made up of various elements, it is necessary, as a matter of convenience and simplicity, that an abbreviated form of chemical language be employed. This has been provided for through a system of symbols, in which the initial letter of the title of the element is generally selected.* In some cases several elements possess the same initial letter; it is then the custom to assign the single letter to the most important, abundant, or earliest-discovered member of the group, and to the others a second letter. Thus, ten names of elements begin with C, this being selected for Carbon, as the most important; then Ca for Calcium, Cd for Cadmium, Ce for Cerium, Cl for Chlorine, Co for Cobalt, and so on. In a few instances the symbols are selected from the old Latin titles of the elements. Thus, Fe is taken from Ferrum (iron), Pb from Plumbum (lead), K from Kalium (potassium), Au from Aurum (gold), and so on.

Atomic Weight or Mass.—The above symbols possess a quantitative signification. Each one represents one atom of the element in question. Thus, Na does not represent any indefinite quantity of sodium, nor Cl any amount of chlorine. These

* See Table of Elements.

symbols, like those of all the other elements, invariably refer to definite and fixed quantities, as in the above instance to 22.88 parts of sodium and 35.18 parts of chlorine, so that NaCl, standing for a molecule of sodium chloride, always denotes 58.06 parts, the sum of one atom of sodium and one atom of chlorine.

The absolute weight of either atoms or molecules cannot be determined directly; hence they are estimated *relatively* by comparison with some standard element. Hydrogen has been selected for this purpose, since it is the lightest known element. Thus, when we say that Na means 22.88 parts of sodium, it also signifies that its atoms are 22.88 times heavier than those of the standard hydrogen, and the atoms of chlorine 35.18 times heavier. The molecule of sodium chloride would then be 58.06 times heavier than a molecule (2 atoms) of hydrogen. *Therefore the atomic weight of an element is the relative weight of its atoms as compared with those of hydrogen as unity.* The molecular weight of an element or compound represents the combined weight of the atoms which make up the molecule.

To determine the atomic weight of an element we must know its relation to hydrogen. Where it forms a compound with this element, analysis of this compound will give us the ratio of weight between the element and hydrogen. If a single atom of each element be present in the compound, as in hydrogen chloride (HCl), this ratio gives us the atomic weight of the chlorine at once; if several atoms of hydrogen are combined with one of the other elements, as in hydrogen oxide (H_2O), the combining ratio does not give the atomic weight of the oxygen until multiplied by the number of the hydrogen atoms ascertained to be present. Where the element the atomic weight of which is desired does not unite directly with hydrogen, we can cause it to combine with some element like chlorine or oxygen, the ratio of which to hydrogen is known, and thus establish the atomic weight by indirect means. Thus, the atomic weights of the metals are generally determined by the analysis of the corresponding chlorides or oxides.

Chemical Formulæ.—The various chemical compounds are produced by the combination of two or more elements, and are graphically represented by placing the symbols of the constituent elements together. Such an aggregation of symbols is designated as a chemical formula. For example, HCl represents a compound made up of one atom of hydrogen (1 part) and one atom of chlorine (35.18 parts); the formula H_2O represents a

compound whose molecule is made up of two atoms of hydrogen (2×1 part $= 2$ parts) and one of oxygen (15.88 parts) : the small figure placed to the right below the symbol of the element hydrogen indicates the number of atoms of that element which enter into the compound.* In unabbreviated style the above formula would be HHO ; for nitric acid it would be HNOOO, while it is written HNO_3. The advantage of such abbreviations is at once apparent.

The formula $2H_2SO_4$ or $2(H_2SO_4)$ represents two molecules of a compound (sulphuric acid) made up of two atoms of hydrogen (2×1 part $= 2$ parts), one of sulphur (31.83 parts), and four of oxygen (4×15.88 parts $= 63.52$ parts). The large numeral (2) placed before the formula is called the *coefficient*, and indicates the number of molecules in the substance represented. The molecular weight of this would be $2\ (2 + 31.83 + 63.52)$ or $2 \times 97.35 = 194.70$ parts. Sometimes this number will apply to only a portion of the symbols. In such a case the latter are enclosed in parentheses. Thus, $Fe_2(SO_4)_3$ represents a compound of two atoms of iron and three groups of SO_4 ; its molecular weight would be calculated thus :

Fe_2	=	55.6 parts $\times$ 2	= 111.2 parts.
SO_4	=	$\begin{cases} S = 31.83 \text{ parts}, \\ O_4 = 63.52 \text{ “ } (15.88 \times 4). \end{cases}$	
$(SO_4)_3$	=	95.35 parts $\times$ 3	= 286.05 “
$Fe_2(SO_4)_3$	=		397.25 parts.

Chemical Equations.—By means of these chemical formulæ we are able to express the various chemical changes which take place between two or more molecules. Such changes are called *reactions*. The several substances taking part in these changes are called *reagents*. In expressing these reactions we employ chemical formulæ, in which the substances entering into the reaction connected by plus (+) signs are placed to the left of the equality sign (=), and the products of the reaction connected by plus signs to the right. Such combinations of formulæ and algebraic signs are called *chemical equations*. Thus, in accordance with the above, the reaction between two molecules, AB and XZ, would be expressed AB + XZ = AZ + BX. Should a minus sign be necessary, it would be ABC

* The term *subscript* is sometimes employed for this figure.

$-B = AC$. The plus sign replaces "and," indicating that the bodies are brought together in reaction ; the equality sign means "produces" or "yields."

Since each symbol entering into a chemical equation represents a definite weight of matter, and the products of the reaction represent an interchange among these symbols, it follows that after the change the quantity of matter must remain the same as before. The sum of the molecular weights of substances on the right of the equality sign must always equal the sum of the molecular weights of those on the left. Thus,—

$AgNO_3$	+	NaCl	=	AgCl	+	$NaNO_3$.
Silver Nitrate.		Sodium Chloride.		Silver Chloride.		Sodium Nitrate.
168.68		58.06		142.29		84.45
226.74				226.74		

This, like all equations, conforms to the rule that when two or more chemical compounds are brought together under proper conditions an interchange of elements takes place, with the formation of new combinations. In the above example the atom of chlorine of the sodium chloride, owing to its greater affinity, attaches itself to the atom of silver, thereby displacing the molecular group* NO_3, which at once attaches itself to the atom of sodium, forming sodium nitrate. The sum of the molecular weights of the products on the right of the equation (226.74) is the same as that on the left (226.74). Not only must the two sides of the equation balance each other quantitatively, but also qualitatively,—that is, all of the elements which enter into the reaction as factors on the left must be accounted for on the right.

Valency of the Elements.—Elements combine with one another because of their attractive force or chemical affinity. For different elements this varies in power, and a measure of it may be had by comparison of the several elements with hydrogen, which combines with the lowest saturating power. This combining or saturating value of an element is termed its *valence* or *equivalence* or *quantivalence*. *Valency is the combining or replacing power of an element expressed in hydrogen units.*

Upon comparing the various compounds of hydrogen with several of the elements, such as chlorine, oxygen, nitrogen,

* For explanation of this term, see Radicals.

sulphur, etc., differences will be observed as regards the number of atoms of hydrogen which combine with these. Thus,—

I.	II.	III.	IV.
HCl	H_2O	H_3N	H_4C
HBr	H_2S	H_3P	H_4Si

From this we see that while chlorine combines with *one* atom of hydrogen, oxygen requires *two*, nitrogen *three*, and carbon *four*. Elements which combine with or replace hydrogen atom for atom are known as *monads;* those of which one atom will combine with or replace two atoms of hydrogen are called *dyads*. Similarly, we have the groups *triads*, *tetrads*, *pentads*, *hexads*, etc. As adjective terms we employ univalent, bivalent, trivalent, quadrivalent, quinquivalent, sexivalent, etc.

Thus, chlorine and bromine, which combine with hydrogen atom for atom, are known as monads, while oxygen and sulphur require two atoms of hydrogen for saturation and are therefore dyads. Sodium, on the other hand, does not combine directly with hydrogen, but, in reacting with hydrogen chloride (hydrochloric acid), replaces hydrogen atom for atom; and so its valence is established, $Na + HCl = NaCl + H$. Similarly the atom of zinc in the reaction with hydrogen chloride displaces two atoms; hence is a dyad, $Zn + 2HCl = ZnCl_2 + H_2$.

Graphic Symbols for Valence.—When it is desired to indicate the valence of an element, a Roman numeral or strokes are placed to the right above the symbol. Thus, O^{II}, N^{III}, P^{V}, or O'', N''', or Cl'. These valence marks are not used ordinarily in writing formulæ or expressing reactions between chemical substances, but only in so-called graphic formulæ. In such instances it is customary to employ lines, called *bonds*, to indicate the linking of atoms to one another. These valence bonds should never be considered as really existing, but merely placed there from pure theoretical considerations.

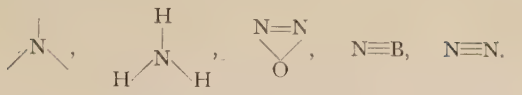
Thus, O= or —O— or O<, N≡ or $-\overset{|}{N}-$, =C= or >C< or $-\overset{|}{\underset{|}{C}}-$.

Examples:

Bivalent Element. O<, $O<\begin{matrix}H\\H\end{matrix}$, $O<\begin{matrix}H\\K\end{matrix}$, O=O,

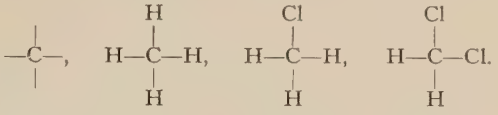
Oxygen Atom. Hydrogen Oxide or Water Molecule. Potassium Hydroxide. Oxygen Molecule. Ozone.

Trivalent Element.



Nitrogen Atom. | Nitrogen Hydride or Ammonia. | Nitrogen Monoxide. | Nitrogen Boride. | Nitrogen Molecule.

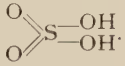
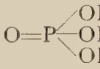
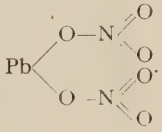
Tetravalent Element.



Carbon Atom. | Methane. | Monochlor-methane. | Di-chlor-methane.

Carbonic Acid Gas. | Hydrocyanic Acid. | Trichlor-methane. | Tetrachlor-methane.

The position of the valence strokes is usually a matter of convenience. They are, however, of great value in illustrating the arrangement and relationship which various atoms bear to one another in the formation of chemical compounds. Such formulæ are usually known as *graphic*, *structural*, or *rational*.

Empirical or Condensed Formulæ.*	Structural or Graphic Formulæ.
Ammonia, NH_3.	
Bismuth Oxide, Bi_2O_3.	
Sulphur Trioxide, SO_3.	
Sulphuric Acid, H_2SO_4.	
Phosphoric Acid, H_3PO_4.	
Lead Nitrate, $Pb(NO_3)_2$.	

* The empirical or condensed formula simply expresses the *kind* and relative number of atoms in the molecule.

Variations in Valency.—The same element may possess a different valence in different compounds. Thus, chlorine, which in combining with hydrogen is a monad, forms a series of compounds with oxygen and hydrogen in which its valence is one, three, five, and seven. Thus,—

Hypochlorous Acid, $H-O-Cl^{I}$.

Chlorous Acid, $H-O-\overset{III}{Cl}=O$.

Chloric Acid, $H-O-\overset{V}{Cl}\begin{matrix}=O\\ \\ =O\end{matrix}$.

Perchloric Acid, $H-O-\overset{VII}{Cl}\begin{matrix}=O\\ =O\\ =O\end{matrix}$.

Sulphur, which combines as a dyad to form hydrogen sulphide, unites with oxygen with the valence of two, four, and six. Thus,—

$H-\overset{II}{S}-H$, $O=\overset{IV}{S}=O$, $O-\overset{VI}{S}(=O)(=O)$.

Hydrogen Sulphide. Sulphur Dioxide. Sulphur Trioxide.

This variation in valence increases by increments of two. Thus, it would be 1, 3, 5, or 7, as in chlorine, bromine, and iodine, or from 3 to 5, as in nitrogen and phosphorus. Among the elements of even valencies they vary, as 2, 4, or 6, as, for example, in sulphur or selenium.

It should be noted, however, that the valency of all the elements towards the monad hydrogen is constant and unchangeable; also when such elements act as electro-negatives (see p. 169) in compounds. Thus, when combined with hydrogen, chlorine, bromine, or iodine is always a monad, or when these are combined with metals, as, for example, copper chloride, $\overset{II}{Cu}Cl_2$, or bismuth chloride, $\overset{III}{Bi}Cl_3$. But when various elements are caused to combine with the dyad oxygen or such other atoms as chlorine or bromine, variations develop.

VALENCY OF ELEMENTS, WITH CLASSIFICATION.

Halogen Group.	Hydrogen.	I.
	Chlorine.	I. (III., V., VII.).
	Bromine.	
	Iodine.	
	Fluorine.	
Oxygen Group.	Oxygen.	II.
	Sulphur.	II. (IV., VI.).
	Selenium.	
	Tellurium.	
Copper Group.	Copper.	II.
	Mercury.	
Tin Group.	Tin.	II., IV.
	Lead.	
	Titanium.	IV.
	Zirconium.	
	Thorium.	
Platinum Group.	Platinum.	II., IV.
	Palladium.	
	Iridium.	
	Osmium, etc.	
Arsenic Group.	Boron.	III.
	Arsenic.	III., V.
	Antimony.	
	Bismuth.	
Nitrogen Group.	Nitrogen.	
	Phosphorus.	
Alkali Metal Group.	Potassium.	I.
	Sodium.	
	Lithium.	
	Rubidium.	
	Cæsium.	
Silver Group.	Silver.	I., III.
	Gold.	
Alkali Earth Group.	Calcium.	II. (IV.).
	Strontium.	
	Barium.	
Magnesium Group.	Magnesium.	II.
	Zinc.	
	Cadmium.	
Iron Group.	Iron.	II. $(Me_2)^{VI.}$
	Nickel.	
	Cobalt.	
Chromium Group.	Chromium.	II., IV., VI.
	Manganese.	
	Molybdenum.	
	Tungsten.	
	Uranium.	
Carbon Group.	Carbon.	IV.
	Silicon.	
Aluminum Group.	Aluminum.	III. $(Al_2)^{VI.}$
	Rare earths.	

Compound Radicals.—From the preceding we have learned that the various elements combine in accordance with their affinities and valency, giving rise to saturated molecules (chemical compounds). Thus, calcium chloride is written $\overset{II}{Ca}\overset{I}{Cl_2}$; it cannot be $CaCl\left(Ca\angle^{Cl}\right)$, for such a compound of chlorine and calcium with a free or unsaturated affinity does not exist. For like reasons potassium oxide must be $\overset{I}{K_2}\overset{II}{O}\left(O\angle^{K}_{K}\right)$, bismuth chloride $\overset{III}{Bi}\overset{I}{Cl_3}\left(Bi\angle^{Cl}_{Cl}{}_{Cl}\right)$, sodium phosphate $\overset{I}{Na_3}\overset{V}{P}\overset{II}{O_4}\left(\overset{II}{O}=P\angle^{O-Na}_{O-Na}{}_{O-Na}\right)$, etc.

For theoretical reasons we find it convenient to distinguish certain unsaturated groups of atoms (with free bonds) which deport themselves like atoms; these are called *compound radicals*, *residues*, or *rests*. Such radicals result from the removal

of an atom from the saturated molecules, their valency being equal to the number of unsaturated bonds. Thus,—

$\overset{II}{H-O-H}$, Hydrogen Oxide.	$\overset{II}{H-S-H}$, Hydrogen Sulphide.	$\overset{III}{H-N=H_2}$, Ammonia.
$-(OH)$, Hydroxyl.	$-(SH)$, Sulphydryl.	$-(NH_2)$, Amidogen.
$\overset{IV}{H-C\equiv H_3}$, Methane.	$\overset{IV}{H-C\equiv N}$, Hydrogen Cyanide.	$\overset{V}{H-NO_3}$, Hydrogen Nitrate.
$-(CH_3)$, Methyl.	$-(CN)$, Cyanogen.	$-(NO_3)$, Nitro-Radical.
$\overset{IV}{O=C=O}$, Carbon Dioxide.		$O=S\begin{matrix}\swarrow O \\ \searrow O\end{matrix}$, Sulphur Trioxide.
$=(CO)$, Carbonyl.	$\overset{V}{\equiv}(P=O)$, Phosphoryl.	$=(SO_2)$, Sulphuryl.

With but few exceptions, the names of these compound radicals terminate in *yl*. Those of an uneven number of free (unsaturated) bonds do not exist in a free state, but, like atoms, when liberated immediately unite with other atoms to form molecules. Thus, $-(OH) + H = HOH(H_2O)$, $-(OH) + -(OH) = HO-OH(H_2O_2)$ hydrogen dioxide, $-(OH) + -(OH) + = (SO_2) = SO_2 \begin{matrix}OH \\ \diagdown OH\end{matrix}$ (H_2SO_4) hydrogen sulphate, $H + -(CH_3) = CH_4$ methane, $Cl + -(CH_3) = CH_3Cl$ methyl chloride, $-(NH_2) + -(CH_3)$ methyl-amine, etc.

Such residues as have an even number of bonds, as sulphuryl $=(SO_2)$ and carbonyl $=(CO)$, may exist in a free state, since there is a mutual saturation between the two free bonds. Thus, $<(SO_2)$, $<(CO)$.

In the various reactions of analytic and synthetic chemistry these radicals play an important part; the readiness with which they interchange with atoms may be seen in the following equations:

$\overset{I}{Ag}\overset{I}{NO_3}$	+	$\overset{I}{Na}\overset{I}{Cl}$	=	$AgCl$	+	$NaNO_3$.	
Silver Nitrate.		Sodium Chloride.		Silver Chloride.		Sodium Nitrate.	
$\overset{I}{CH_3}\overset{I}{I}$	+	$\overset{I}{Ag}\overset{I}{OH}$	=	CH_3OH	+	AgI.	
Methyl Iodide.		Silver Hydroxide.		Methyl Hydroxide.		Silver Iodide.	
$\overset{I}{Na_2}\overset{II}{SO_4}$	+	$\overset{II}{Ba}(\overset{I}{NO_3})_2$	=	$2NaNO_3$	+	$BaSO_4$.	
Sodium Sulphate.		Barium Nitrate.		Sodium Nitrate.		Barium Sulphate.	
$2\overset{I}{Na_3}\overset{III}{PO_4}$	+	$3\overset{II}{Mg}\overset{II}{SO_4}$	=	$3Na_2SO_4$	+	$\overset{II}{Mg_3}(\overset{III}{PO_4})_2$.	
Sodium Phosphate.		Magnesium Sulphate.		Sodium Sulphate.		Magnesium Phosphate.	

Laws governing Chemical Combination.

A study of the phenomena of chemical action demonstrates that chemical combination invariably takes place in conformity with certain laws.

Lavoisier's Law of the Indestructibility of Matter.—According to Lavoisier, whenever matter is apparently destroyed it continues to exist in another form. Transformations are constantly taking place in nature, but do not involve any increase or decrease in the total amount of matter. The law is, *whenever a change in the composition of a substance takes place, the amount of matter after the change is the same as before.* For example, the gaseous products of the combustion of a candle—namely, water and carbonic anhydride—will weigh exactly the same as the candle itself, allowing, of course, for the oxygen necessary to the combustion.

Dalton's Law of Definite Proportions (by Weight).—*Each element combines with the others in a fixed and definite proportion by weight.*

If we mix equal weights of sulphur and iron, we will find that after chemical union has taken place some sulphur remains uncombined, while if an excess of iron has been used, some of this will remain behind. If we continue experiments, we will finally find that when the two elements are mixed in the proportions of 7 parts by weight of iron ($\frac{1}{8}$ of 56) and 4 parts by weight of sulphur ($\frac{1}{8}$ of 32), which represent their combining or atomic weights, the combination is perfect, neither iron nor sulphur being left. For like reasons, *one* part by weight of hydrogen unites with 35.18 parts by weight of chlorine, 79.34 parts of bromine, and 126.89 parts of iodine; 35.18 parts by weight of chlorine combine with 22.88 parts by weight of sodium and 107.11 parts of silver.

Dalton's Law of Multiple Proportions (by Weight).—*When two elements unite in several different proportions, the highest proportions are invariably multiples of the lowest.*

As instances of the application of this law the following examples are cited:

Carbon forms *two* compounds with oxygen; the combining proportions are parts by weight:*

	Carbon.	Oxygen.	
Carbon Mon-oxide . .	12 parts,	16 parts	$= 16 \times 1 = CO.$
Carbon Di-oxide . . .	12 "	32 "	$= 16 \times 2 = CO_2.$

Oxygen forms *five* compounds with nitrogen according to the following proportions by weight:

* The atomic weights of carbon, oxygen, and nitrogen have been rounded off for the sake of convenience.

	Nitrogen.	Oxygen.	
Nitrogen Mon-oxide . .	28 parts,	16 parts	$= 16 \times 1 = N_2O$.
Nitrogen Di-oxide . . .	28 "	32 "	$= 16 \times 2 = N_2O_2$.
Nitrogen Tri-oxide . .	28 "	48 "	$= 16 \times 3 = N_2O_3$.
Nitrogen Tetr-oxide . .	28 "	64 "	$= 16 \times 4 = N_2O_4$.
Nitrogen Pent-oxide . .	28 "	80 "	$= 16 \times 5 = N_2O_5$.

It must be distinctly understood that only whole atoms, and not fractions, can combine. Thus, no compound can be formed from 28 parts of nitrogen and 24 parts ($16 \times 1\frac{1}{2}$) of oxygen. Any quantities above or below the given multiples do not combine, but remain as free oxygen or nitrogen.

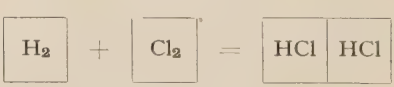
Laws of Combination by Volume.—The proportions in which gaseous volumes enter into combination were first determined by Gay-Lussac, who formulated the following law of two clauses :

1. *The ratio in which gases combine by volume is always a simple one.*

2. *The volume of the gaseous product obtained in a combination bears a simple ratio to the volumes of its constituents.*

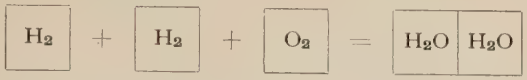
The applications of these laws are illustrated in the formation of certain typical hydrogen compounds.

(*a*) If a concentrated aqueous solution of hydrogen chloride (HCl) be subjected to electrolysis, we will find that equal volumes of chlorine and hydrogen gases are liberated. This establishes the fact that, analytically, hydrogen chloride is made up of the two elementary gases hydrogen and chlorine combined in equal volumes. If, on the other hand, equal volumes of hydrogen and chlorine are mixed and caused to combine by means of the electric spark, 2 volumes of hydrogen chloride (a gas) result, exactly the sum of the volumes of the constituents. Thus, 1 vol. $H + 1$ vol. $Cl = 2$ vol. HCl.

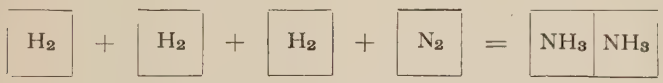


(*b*) On subjecting water (H_2O) to the same analytic process of electrolysis, 1 volume of oxygen gas and 2 volumes of hydrogen gas are obtained. To prove the accuracy of this synthetically, if 100 cubic centimeters (2 volumes) of hydrogen and 50 cubic centimeters (1 volume) of oxygen are caused to combine by means of the electric spark, the resulting water-

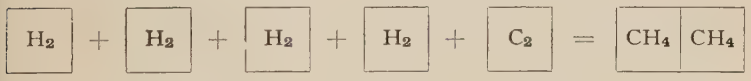
vapor (steam) measures 100 cubic centimeters (2 volumes). Thus, 2 vol. H + 1 vol. O = 2 vol. vapor H_2O.



(*c*) Upon subjecting ammonia gas (NH_3) to analysis, we find the proportion of nitrogen and hydrogen gases obtained as 1 to 3. The volume of ammonia being doubled by the decomposing action of the electrical current, 100 cubic centimeters of the gas yield 200 cubic centimeters of mixed gases, of which 50 cubic centimeters represent nitrogen and 150 represent hydrogen. On mixing 3 volumes of hydrogen and 1 volume of nitrogen and causing them to combine by means of an electric spark, 2 volumes of ammonia gas result. Thus, 3 vol. H + 1 vol. N = 2 vol. NH_3.



(*a*) Through the same method of analysis* we find that 4 vol. H + 1 vol. C vapor = 2 vol. CH_4, methane.



The volumes of the gaseous products are invariably *two*, regardless of the fact that the sum of the volumes entering the reaction is more.

Relation of Density to Molecular and Atomic Weight.—If, according to the laws of Dalton, the different proportions by weight in which bodies combine represent the relative weights of their atoms or multiples of these, and these same elements combine in definite and simple proportions by volume (Gay-Lussac), it would follow that the weight of equal volumes of gases must bear the same relation to one another as their atomic weights. This is true for simple gases only, and on comparing their densities (H being taken as unit) we will find that the same figure expresses both the atomic (combining) weight and density, as will be seen in the following table :

* A synthesis is impossible because carbon cannot be obtained in vapor form, yet this assumption is in accordance with the analysis of this and many other compounds of carbon.

Elements.	Density (H = 1).	Atomic Weights.
Hydrogen	1	1
Oxygen	15.88	15.88
Nitrogen	13.93	13.93
Sulphur	31.83	31.83
Chlorine	35.18	35.18
Bromine	79.34	79.34
Iodine	125.89	125.89

Therefore the densities of the gasified elements are equal to their atomic weights.

The molecular weights of compound bodies are obtained by adding together the weights of the constituent atoms. Thus, the hydrogen molecule, containing 2 atoms, would weigh 2 ; that of hydrogen chloride, containing 1 hydrogen atom and 1 chlorine atom, would weigh 1 + 35.18, or 36.18. Since gas densities of elements are equal to their atomic weights, those of compound bodies would be one-half of their molecular weight ; that of hydrogen chloride would be 18.09.

The rule that the molecular weight of a compound body is equal to twice its gas density is based on the law of Avogadro,— namely, *in equal volumes of all gases there is an equal number of molecules.* Each 1 molecule of a gas or vapor occupies 2 volumes* (1 atom of hydrogen occupying 1 volume) ; the weight of these 2 volumes is double the density compared with hydrogen, for density is the weight of 1 volume of the gas in question compared with the weight of 1 volume of hydrogen. To find the weight of the molecule (weight of 2 volumes) of a gas or vapor, we multiply its density (weight of 1 volume) by 2. This relationship will be seen in the following table :

	Atomic Weights.	Density.	Molecular Weights.
Hydrogen	H = 1	1	H_2 = 2
Chlorine	Cl = 35.18	35.18	Cl_2 = 70.36
Hydrogen Chloride		18.09	HCl = 36.18
Oxygen	O = 15.88	15.88	O_2 = 31.76
Hydrogen Oxide		8.94	H_2O = 17.88
Hydrogen Sulphide		16.91+	H_2S = 33.83
Nitrogen	N = 13.93	13.93	N_2 = 27.86
Nitrogen Hydride		8.46+	NH_3 = 16.93
Phosphorus	P = 30.75	61.50	P_4 = 123.
Hydrogen Phosphide		16.87+	PH_3 = 33.75

* 1 vol. H + 1 vol. Cl = 2 vol. HCl.
2 " H + 1 " O = 2 " H_2O.
3 " H + 1 " N = 2 " NH_3.
4 " H + 1 " C = 2 " CH_4.

In order to ascertain the molecular weight of solid compound bodies, it is necessary that we be able to vaporize them without decomposition. Knowing the molecular weight of a chemical compound, the relative atomic weights are readily established by analysis.

Conditions Necessary for Chemical Combination.— In order to bring about chemical action between two or more substances, the first condition necessary is to secure a sufficiently intimate contact between the molecules, so as to favor an exchange between their several atoms. If the reacting substances are solids, combination takes place in a few instances by reducing both to a very fine powder and mixing ; in most such cases it is necessary to assist the reaction by heat. It is usually the custom, however, to secure molecular contact between the compounds by aid of a solvent ; thus, we may mix finely powdered corrosive sublimate ($HgCl_2$) and potassium iodide (KI), and as long as they remain in the dry condition no action will take place, but with the addition of water the white powder disappears and a red one forms, thereby indicating that chemical action, resulting from an interchange of the several atoms, has taken place.

$HgCl_2$	+	$2KI$	=	HgI_2	+	$2KCl$.
Mercuric Chloride.		Potassium Iodide.		Mercuric Iodide.		Potassium Chloride.

In gases we find the same freedom of molecular contact and motion as in the solutions of solids. Thus, on mixing chlorine and gaseous hydrogen bromide, bromine is liberated from its compound with hydrogen : $2Cl + 2HBr = 2HCl + 2Br$.

Nitrogen dioxide unites under like circumstances with oxygen to form nitrogen tetroxide, $N_2O_2 + O_2 = N_2O_4$.

Chemical combination between chlorine and hydrogen may be accomplished by exposing the mixture to strong sunlight.

In other instances chemical union between different gases is induced only through the assistance of the electric spark. Very intimate contact, with union of gaseous bodies, may be brought about by means of a finely divided metal, as platinum sponge ;* for, on passing a mixture of sulphur dioxide and oxygen over this, chemical combination results and sulphur trioxide is produced.

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* Asbestos wool is impregnated with a solution of ammonio-platinic chloride, then ignited, whereby finely divided platinum remains distributed over the asbestos.

Chemical Changes in Aqueous Solutions.—Upon mixing solutions of chemical compounds, an interchange of atoms takes place, resulting in the formation of new compounds ; precipitation takes place or not, according to the solubility of these in the given menstruum.

Example.—If we mix an almost colorless solution of ferric chloride and a colorless solution of sodium acetate, a dark red solution results. This change in color is indicative of chemical action, although no precipitation takes place.

$$\underset{\text{Ferric Chloride.}}{FeCl_3}^{*} + \underset{\text{Sodium Acetate.}}{3(NaC_2H_3O_2)} = \underset{\text{Sodium Chloride.}}{3NaCl} + \underset{\text{Ferric Acetate.}}{Fe(C_2H_3O_2)_3}.$$

Example.—If we mix solutions of barium chloride and sodium sulphate, a precipitate forms, owing to the insolubility of the newly formed compound barium sulphate, which is the result of an interchange or rearrangement of atoms. Thus,—

$$\underset{\text{Barium Chloride.}}{BaCl_2} + \underset{\text{Sodium Sulphate.}}{Na_2SO_4} = \underset{\text{Barium Sulphate.}}{BaSO_4} + \underset{\text{Sodium Chloride.}}{2NaCl}.$$

In this manner the element barium may be removed from a solution by the aid of a reagent, with which it forms an insoluble compound. This same is true of most all elements, and furnishes the analyst with a valuable means for their identification and separation.

Example.—If the resulting compounds formed in a reaction of this kind are soluble in the solvent, we must resort to artificial means of removing either the undesirable or the desirable product. This is usually accomplished either by changing the temperature or the solvent, whereby one of either of the products precipitates. Thus, we may prepare ammonium bromide by mixing solutions of potassium bromide and ammonium sulphate ; as a result, two soluble compounds are produced, as follows :

$$\underset{\text{Potassium Bromide.}}{2KBr} + \underset{\text{Ammonium Sulphate.}}{(NH_4)_2SO_4} = \underset{\text{Ammonium Bromide.}}{2NH_4Br} + \underset{\text{Potassium Sulphate.}}{K_2SO_4}.$$

In order to separate the inert side-product potassium sulphate from the ammonium bromide, advantage is taken of the fact that the former is practically insoluble in diluted alcohol, while the latter is soluble ; hence alcohol is added to the not too dilute fluid mixture, and after standing in a cool place a few hours the

* The most recent determinations of the vapor density of ferric chloride accord with the formula $FeCl_3$. However, the older customary double formula Fe_2Cl_6 ($Cl_3{\equiv}Fe{-}Fe{\equiv}Cl_3$) is still retained elsewhere in the work.

solution of the ammonium bromide is drained off from the precipitated sulphate and evaporated.

The following general rules of solubility should be noted, for a knowledge of these is indispensable for laboratory work :

1. All normal* nitrates are soluble.

2. All chlorides are soluble except those of silver, mercurous-mercury, cuprous chloride, and lead.

3. All sulphates are soluble except those of barium, calcium, strontium, and lead.

4. All phosphates are insoluble except those of the alkali metals (viz., K, Na, Li) and ammonium.

5. All carbonates are insoluble except those of the alkali metals and ammonium.

Influence of Various Forms of Energy upon Chemical Affinity.—As already stated, chemical affinity or attraction may vary not only between different bodies, but also, under the influence of such forces as heat, light, and electricity, it may increase or decrease in intensity, or cease altogether in the same substance.

Heat.—The effect of temperature change upon chemical attraction may be threefold : first, at very low temperatures chemical affinity ceases entirely ; second, moderate temperatures up to certain limits, as a general rule, assist chemical union ; third, sufficiently high temperatures cause a breaking up of chemical compounds into simpler ones.

The degree of temperature which governs the increase or decrease of affinity varies with different bodies. For example, mercury when exposed to the air at ordinary temperature undergoes but little change, but if it be heated to near its boiling point (360° C.) it readily unites with the oxygen of the air, forming red mercuric oxide (HgO); if this temperature be increased to 400° C., further attraction between these elements ceases, and the compound decomposes into oxygen and mercury.

Again, such compounds as ammonium chloride (NH_4Cl) and phosphorus pentachloride (PCl_5), when heated to high temperatures, are broken up into simpler compounds,—the former into gaseous ammonia (NH_3) and hydrogen chloride (HCl), the latter into phosphorus trichloride (PCl_3) and chlorine (Cl_2). Such a phenomenon is called *dissociation*,—that is, a partial

* For explanation of this term, see p. 175.

decomposition or breaking up of the molecules of a chemical compound. This increases with the temperature. Thus, with water it begins at 1000° C., and is not complete until the temperature reaches about 2500° C.

The density of sulphur vapor at 500° C. gives this element an atomic weight of 96, there being 6 atoms to the molecule; at 1000° C. these more complex hexatomic molecules dissociate or break up further into simpler diatomic molecules,—that is, the molecule contains 2 atoms, which gives the accepted atomic weight of S = 32.

Light.—Like heat, light also exerts an influence upon chemical combination and decomposition, according to the nature of the substance or elements. Such gases as chlorine and hydrogen, when mixed and exposed to the direct rays of the sun, unite with explosive violence. Under similar conditions, or even in diffused light, the chlorine gas of chlorine water unites with the hydrogen of the water to form hydrogen chloride. Thus, $Cl_2 + H_2O = 2HCl + O$.

Chemical decomposition of aqueous solutions of hydrogen iodide or bromide readily takes place on exposure to light, with separation of iodine or bromine, according to the following equation: $2HI + O = H_2O + I$. The yellow iodide of mercury, under like conditions, changes to a dark green, the light having caused a separation of a portion of the mercury from the iodine. The decomposition of the compounds of iodine and bromine with silver by the action of light is the principle upon which the art of photography is based.

Electricity.—By the action of the induction spark chemical union among the various gaseous elements may readily be brought about. As, for example, hydrogen and oxygen unite to form water, chlorine and hydrogen form hydrogen chloride.

Where, on the one hand, chemical union may be brought about, it is, on the other, destroyed through the same influence. Thus, on passing the galvanic current through solutions of the above compound gases, they may again be resolved into their elements.

Such decompositions by the electric current are called *electrolytic*, or the operation as that of *electrolysis*. In order to secure such decompositions by the galvanic current, it is necessary that the substance (*electrolyte*) should be either in the gaseous, liquid, or fused condition. The products of electrical decomposition are known as *ions*, those separating at the positive (+)

pole, or anode, are called *anions*, while those which collect at the negative (—) pole, or cathode, are the *cations*.

Upon subjecting various compounds of the elements, either in solution or fused condition, to the action of the galvanic current, the metallic elements are always attracted to the cathode, and are known as electro-positive, while the non-metallic elements, as oxygen, sulphur, iodine, phosphorus, etc., are attracted to the anode, and classed as electro-negative. Thus,—

1. HCl + electric current = H (at $\overset{-}{\text{cathode}}$) + Cl (at $\overset{+}{\text{anode}}$).
   Hydrogen Chloride.
2. $PbBr_2$ + " " = Pb " + Br_2 "
   Lead Bromide.
3. $ZnSO_4$ + " " = Zn " + SO_4 "
   Zinc Sulphate.

In Equation 3 the electro-positive zinc separates in metallic form at the negative pole, while the electro-negative radical (SO_4) would be presumed to separate at the positive pole. However, since this radical is incapable of existing in free condition, a secondary reaction takes place with the water present in the solution. Thus,—

$$\underset{\text{Sulphuryl.}}{=SO_4} + H_2O = \underset{\substack{\text{Hydrogen}\\\text{Sulphate.}}}{H_2SO_4} + O.$$

The reaction, to be complete, should be written as follows :

$ZnSO_4 + H_2O$ + current = Zn (— pole) + H_2SO_4 + O (+ pole).

4. NaCl + electric current = Na (at cathode) + Cl (at anode).

The electro-positive metal sodium separates at the cathode. However, a secondary reaction sets in immediately between this metal and the water present, whereby hydrogen gas is liberated according to the equation :

$$\underset{\text{Sodium.}}{2Na} + \underset{\text{Water.}}{2(HOH)} = \underset{\text{Sodium Hydroxide.}}{2(NaOH)} + \underset{\text{Hydrogen.}}{H_2}.$$

The complete reaction is expressed thus :

$$2NaCl + 2HOH + \text{current} = \underset{\text{Cathode.}}{2NaOH + H_2} + \underset{\text{Anode.}}{Cl_2}.$$

Electro-Chemical Series.—According to their electrical deportment, the various elements may be arranged into a series

in which those elements of the most intense positive characters are placed at one extremity, while the negative constitute the other, their activity diminishing towards the centre.

—O, S, Se, N, F, Cl, Br, I, P, As, Cr, Mo, B, C, Sb, Si, H, Au, Pt, Hg, Ag, Cu, Bi, Sn, Pb, Co, Ni, Fe, Zn, Mn, Al, Mg, Ca, Sr, Ba, Li, Na, K, Rb.+

Each element in this series * is electro-negative to those following and electro-positive to those preceding. Thus, phosphorus is negative to Zn($\overset{+}{Zn_3}\overset{-}{P_2}$) and positive to oxygen ($\overset{+}{P_2}\overset{-}{O_5}$).

This series table is of value in explaining in a general way differences in the intensity of affinity between various elements, also the formation of compound molecules, such as acids, bases, and salts.

Ionic Theory.—According to modern investigations, the electric current is not the direct cause of the above decompositions, but it simply exerts a selective influence over the constituents which have already undergone separation in the operation of solution. For example, when salts, bases, or acids are dissolved in water, they are assumed to dissociate (split up) more or less into their ions.† Thus, sodium chloride is split up into electro-positive sodium (+ Na) ions and electro-negative chlorine (— Cl) ions. These ions are charged with electricity, and yield this the instant they are transported to the electrodes. Where a normal sodium atom would cause an instantaneous decomposition of water, a charged atom is neutral, and remains so until its electrical charge has been removed by contact with the negative electrode.

The greater the dilution the more complete is this dissociation. Further, potassium nitrate (KNO_3) in solution ionizes into K (+) and NO_3 (—) ions, sulphuric acid into H_2 (+) and SO_4 (—) ions, sodium hydroxide into Na (+) and OH (—) ions. Since dilute aqueous solutions of electrolytes contain the greater portion of their ions in free condition, the properties of these compounds are dependent upon those of its free ions. This theory of ionic condition explains the ready interchangeability between the molecules of different compounds when brought into contact with one another in solution. Thus,—

* This list includes only the more important elements.

† Faraday was the first to apply the name *ions* to atoms or groups of atoms which are liberated by the action of the electric current upon an electrolyte.

$\overset{+}{Cu}\overset{-}{SO_4}$	+	$\overset{+}{2K}\overset{-}{OH}$	=	$\overset{+}{Cu}\overset{-}{(OH)_2}$	+	$\overset{+}{K_2}\overset{-}{SO_4}$.
Copper Sulphate.		Potassium Hydrate.		Copper Hydroxide (Insoluble).		Potassium Sulphate.
$\overset{+}{Ag}\overset{-}{NO_3}$	+	$\overset{+}{K}\overset{-}{ClO_3}$	=	$\overset{+}{Ag}\overset{-}{ClO_3}$	+	$\overset{+}{K}\overset{-}{NO_3}$.
Silver Nitrate.		Potassium Chlorate.		Silver Chlorate (Insoluble).		Potassium Nitrate.

The compounds of carbon (organic) do not ionize.

Compound Molecules.

Compound molecules result from the union of unlike atoms. These may be divided into two classes : (1) *Binary* compounds are molecules containing only two kinds of atoms, and these are directly united; as, for example, NaCl, H_2O, MgO. (2) *Ternary* compounds contain three or more different kinds of atoms ; one of these serves to unite the other dissimilar atoms ; for example,

$$H_2SO_4\left(\begin{matrix}HO\\HO\end{matrix}\!>\!S\!\!<\!\!\begin{matrix}O\\O\end{matrix}\right),\quad KNO_3\left(K\!-\!O\!-\!N\!\!<\!\!\begin{matrix}O\\O\end{matrix}\right),\quad CaCO_3\left(\begin{matrix}C\!<\!\begin{matrix}O\\O\end{matrix}\\\quad\quad O\end{matrix}\!>\!Ca\right).$$

Acids.—Acids are compounds of hydrogen with an electronegative element or group of elements. They may also be defined as salts of hydrogen. These usually, when diluted, possess a sour taste, redden blue litmus, and saturate bases (oxides and hydroxides of metals). All acids contain hydrogen, which is readily replaceable by metals. Thus,—

a.	$2HCl$	+	Zn	=	$ZnCl_2$	+	H_2.	
	Hydrogen Chloride.		Zinc.		Zinc Chloride.		Hydrogen.	
b.	$2HCl$	+	ZnO	=	$ZnCl_2$	+	H_2O.	

When hydrogen chloride (hydrochloric acid) is brought into contact with a metal with which it is capable of reacting, hydrogen gas is liberated and its place is taken by the metal. If, instead of a metal, a metallic oxide (an oxygen compound of the metal) is employed, water separates as by-product.

Acids may be divided into two classes,—namely, *hydrogen* or *binary acids* and *oxy-* or *ternary acids.*

Hydrogen or Haloid or Binary Acids.—These are compounds of hydrogen with the halogens ;* as, for example,—

HCl = Hydrogen chloride or hydrochloric acid.
HBr = Hydrogen bromide or hydrobromic acid.
HI = Hydrogen iodide or hydriodic acid.
HF = Hydrogen fluoride or hydrofluoric acid.

* The term *halogen* refers to the elements chlorine, bromine, iodine, and fluorine.

Oxy- or Ternary Acids.—These are compounds of hydrogen united by means of oxygen to one or more negative atoms or radicals ; as examples we have

$HNO_3\left(HO—N\begin{matrix}O\\O\end{matrix}\right)$, hydrogen nitrate or nitric acid.

$H_2SO_4\left(\begin{matrix}HO\\HO\end{matrix}>S\begin{matrix}O\\O\end{matrix}\right)$, hydrogen sulphate or sulphuric acid.

$H_3PO_4\left(O=P\begin{matrix}OH\\OH\\OH\end{matrix}\right)$, hydrogen phosphate or phosphoric acid.

Basicity.—The basicity of acids is represented by the *number* of hydrogen atoms which can be replaced by positive atoms of the elements. Thus, we have as examples of

Monobasic acids, hydrogen chloride (HCl), hydrogen bromide (HBr), and hydrogen nitrate (HNO_3), which contain only *one* atom of displaceable hydrogen.

Dibasic acids, hydrogen sulphate (H_2SO_4) and hydrogen oxalate ($H_2C_2O_4$). *Two* atoms of hydrogen here are displaceable by such positive atoms as sodium (Na) or potassium (K).

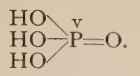
Tribasic acids, hydrogen phosphate (H_3PO_4) and hydrogen arsenate (H_3AsO_4). These acids contain *three* atoms of hydrogen which are replaceable.

Tetrabasic acids, hydrogen pyrophosphate ($H_4P_2O_7$) and hydrogen ferrocyanide ($H_4Fe(CN)_6$). Here *four* atoms are replaceable.

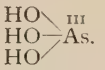
Acids of a greater basicity than unity are generally termed *polybasic*,—that is, all of the above acids, excepting monobasic, belong to this class. Among the ternary or oxy-acids the number of hydrogen atoms contained in the molecule is not always an indication of its basicity. The replaceable hydrogens are all linked to the negative atom or group by aid of oxygen ; hence the number of hydroxyl (OH) groups determines this. Thus, hypophosphorous acid, $O=P\begin{matrix}H\\H\\OH\end{matrix}$, contains three hydrogen atoms ; however, since there is but one hydroxyl group present, it is monobasic. For like reasons phosphorus acid, $O=P\begin{matrix}H\\OH\\OH\end{matrix}$, is dibasic.

Ortho-, Meta-, and Pyro- Acids.—*Ortho*-acids are those in which there is the same number of hydroxyl (OH) groups

as there are affinities or valencies in the negative atom or group. Thus,—

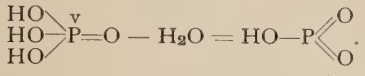


Ortho-phosphoric Acid (H_3PO_4).

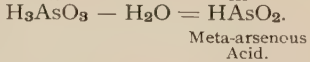


Ortho-arsenous Acid (H_3AsO_3).

By the removal of one molecule of water (H_2O), derivatives containing but one atom of hydrogen result. These are called *meta*-acids. Thus,—

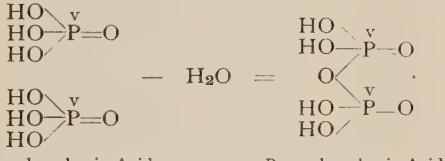


Meta-phosphoric Acid.



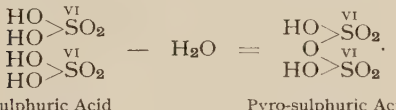
Meta-arsenous Acid.

If we remove one molecule of water from two molecules of an ortho-acid, a *pyro*-acid results,—



Ortho-phosphoric Acid ($2(H_3PO_4)$).

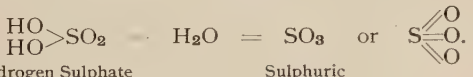
Pyro-phosphoric Acid ($H_4P_2O_7$).



Sulphuric Acid ($2H_2SO_4$).

Pyro-sulphuric Acid ($H_2S_2O_7$).

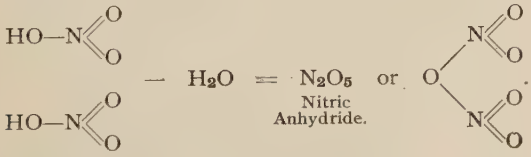
Acid Anhydrides (from α and $\dot{\upsilon}\delta\omega\rho$ = *without water*). These are obtained from acids by removing all of the hydrogen with sufficient oxygen to form water (H_2O). Thus,—



Hydrogen Sulphate (H_2SO_4).

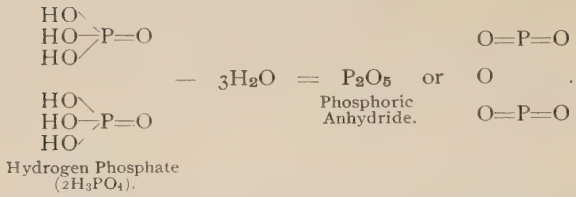
Sulphuric Anhydride.

In case the number of hydrogen atoms in the acid is uneven, the anhydride is derived from two molecules of the acid. Thus,—



Hydrogen Nitrate ($2HNO_3$).

Nitric Anhydride.



These anhydrides unite with water to form their respective acids.

Bases.—These are compounds in which a metal is linked by oxygen to hydrogen. Or they may be considered as being derived from one or more molecules of water (HOH), in which one hydrogen of each is replaced by an electro-positive element. Owing to the presence of the hydroxyl group (—OH), these compounds are known as hydroxides (sometimes incorrectly called hydrates). As examples we have

Potassium hydroxide, K—OH.

Barium hydroxide, $Ba<^{OH}_{OH}$.

Bismuth hydroxide, $Bi(OH)_3$.

Aluminum hydroxide, $Al_2(OH)_6$.

The number of OH groups present determines also the saturating* power of the base, which is called the acidity of the base. Thus, KOH is mon-acid, $Ba(OH)_2$ di-acid, $Bi(OH)_3$ tri-acid, etc. Such bases as contain two or more hydroxyl groups are known as polyhydroxides.

With oxygen, the metals usually yield oxides, and many of these form hydroxides or bases when brought in contact with water:

$$\underset{\text{Sodium Oxide.}}{Na_2O} + H_2O = \underset{\text{Sodium Hydroxide.}}{2NaOH}.$$

$$\underset{\text{Calcium Oxide.}}{CaO} + H_2O, = \underset{\text{Calcium Hydroxide.}}{Ca(OH)_2}.$$

The hydroxides of the alkalies (K, Na, Li, (NH_4)) and of the alkali earths (Ba, Ca, Mg, Sr) have a strong alkaline (like lye)

* For explanation of this term, see under Acids.

taste, and restore litmus reddened by acids to its natural blue color.

Salts.—These are compounds formed by the union of acids and bases, or by replacing the hydrogen of an acid by a metal. Salts consist of two parts, one being electro-positive and the other electro-negative. Thus,—

$\overset{+}{Na}\overset{-}{OH}$	+	$\overset{+}{H}\overset{-}{Cl}$	=	$\overset{+}{Na}\overset{-}{Cl}$	+	H_2O.				
Sodium Hydroxide.		Hydrogen Chloride.		Sodium Chloride.		Water (Hydrogen Oxide).				
$\overset{+}{Ba}\overset{-}{(OH)_2}$	+	$2H\overset{+}{-}Cl$	=	$\overset{+}{Ba}\overset{-}{Cl_2}$	+	$2H_2O$.				
Barium Hydroxide.				Barium Chloride.						
$\overset{+}{Bi}\overset{-}{(OH)_3}$	+	$3H\overset{+}{-}Cl$	=	$\overset{+}{Bi}\overset{-}{Cl_3}$	+	$3H_2O$.				
Bismuth Hydroxide.				Bismuth Chloride.						
$\overset{+}{Na_2}\overset{-}{O}$	+	$\overset{+}{H_2}\overset{-}{SO_4}$	=	$\overset{+}{Na_2}\overset{-}{SO_4}$	+	H_2O.				
Sodium Oxide.		Hydrogen Sulphate.		Sodium Sulphate.						
$\overset{+}{Ca}\overset{-}{CO_3}$	+	$2H\overset{+}{-}NO_3$	=	$\overset{+}{Ca}\overset{-}{(NO_3)_2}$	+	H_2O	+	CO_2.		
Calcium Carbonate.		Hydrogen Nitrate.		Calcium Nitrate.				Carbon Dioxide.		

The above reactions also serve to illustrate what is known as *neutralization*,—that is, the exact saturation of an acid with an alkali, alkali hydroxide, or carbonate. The completeness of this neutralization (replacement of hydrogen) is readily ascertained by the effect of the solution on the color of litmus. Excess of acid changes this to red, while alkalies cause its restoration to blue. Salts also result from the action of acids on metals, and instead of water being a side product, as in the preceding examples, gases are liberated.

Zn	+	H_2SO_4	=	$ZnSO_4$	+	H_2.				
Zinc.		Hydrogen Sulphate.		Zinc Sulphate.		Hydrogen.				
$3Cu$	+	$8HNO_3$	=	$3Cu(NO_3)_2$	+	N_2O_2	+	$4H_2O$.		
Copper.		Hydrogen Nitrate.		Copper Nitrate.		Nitrogen Dioxide.				

Salts of the oxygen or ternary acids are classified as *normal*, *acid*, or *basic*. Inasmuch as there is only one replaceable hydrogen in the binary acids, there can be only one class of salts.

Normal Salts.—These are formed by the replacement of *all* of the hydrogen of an acid by an equivalent amount of metal. Thus,—

Acids.		Normal or Neutral Salts.	
Hydrogen nitrate,	HNO_3.	Sodium nitrate,	$NaNO_3$.
Hydrogen sulphate,	H_2SO_4.	Sodium sulphate,	Na_2SO_4.
Hydrogen phosphate,	H_3PO_4.	Sodium phosphate,	Na_3PO_4.

These normal salts are sometimes designated as neutral salts because of the complete neutralization or replacement of the acid hydrogen. Such salts do not alter the color of litmus solution.

Acid Salts.—These are derived by the partial replacement of the hydrogen of polybasic acids by metals. Such salts turn blue litmus red because of their acid character, there being still some free unreplaced hydrogen of the acid. Thus,—

Acids.	Acid Salts.
Hydrogen sulphate, H_2SO_4.	Sodium acid, $NHSO_4$, or hydrogen sulphate.
Hydrogen oxalate, $H_2C_2O_4$.	Sodium acid, $NaHC_2O_4$, or hydrogen oxalate.

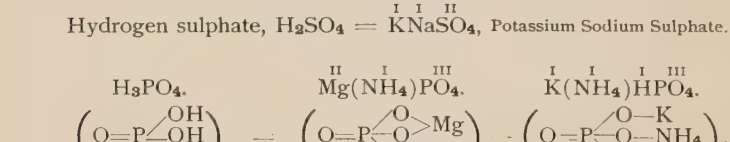
In the tribasic acids we have three replaceable hydrogens, hence two acid salts. Thus,—

H_3PO_4.	NaH_2PO_4.	Na_2HPO_4.	Na_3PO_4.
Hydrogen Phosphate.	Mono-sodium-di-hydrogen Phosphate. Mono-basic Sodium Phosphate. Primary Sodium Phosphate.	Di-sodium-mono-hydrogen Phosphate. Di-basic Sodium Phosphate. Secondary Sodium Phosphate.	Tri-sodium Phosphate. Tri-basic Sodium Phosphate. Tertiary Sodium Phosphate.

Double Salts.—These are obtained by replacing the hydrogen atoms of polybasic acids by different positive atoms. Thus,—

Hydrogen sulphate, $H_2SO_4 = \overset{I}{K}\overset{I}{Na}SO_4$, Potassium Sodium Sulphate.

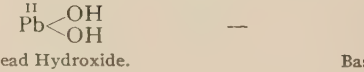
H_3PO_4. — $\overset{II}{Mg}(\overset{I}{NH_4})\overset{III}{PO_4}$. — $\overset{I}{K}(\overset{I}{NH_4})\overset{I}{H}\overset{III}{PO_4}$.



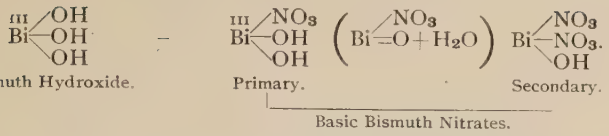
Hydrogen Phosphate. — Magnesium Ammonium Phosphate. — Potassium Ammonium Phosphate.

Hydrogen silicate, H_4SiO_4. — $Ba''Zn''SiO_4$, Baro-zincic silicate.

Basic Salts.—These are derived by the replacement of not all the hydroxyl groups of polyhydrates by acid residues. Thus,—



Lead Hydroxide. — Basic Lead Nitrate.



Or these basic salts may be considered as resulting from the replacement of hydrogen atoms of an acid by oxide or hydroxide rests. Thus,—

HNO_3 — $(PbOH)NO_3$ or $Pb(OH)NO_3$. $(BiO)NO_3$ or $Bi(O)NO_3$.

Hydrogen Nitrate. Basic Lead Nitrate. Basic Bismuth Nitrate.

HCl — $(ZnOH)Cl$ or $Zn(OH)Cl$.

Hydrogen Chloride. Basic Zinc Chloride.

Nomenclature.

Chemical nomenclature is intended to indicate in a systematic manner the composition of compound bodies.

In binary compounds, which consist of molecules made up of two elements, the positive element is placed first, followed by the negative. Thus, we write $\overset{+}{Na}\overset{-}{Cl}$, and not $\overset{+}{Cl}\overset{-}{Na}$. In naming the compound, the same order is observed, the last syllable terminating in "*ide*." Thus,—

$\overset{+}{Na}\overset{-}{Cl}$ = Sodium chlor*ide*.

$\overset{+}{Ca}\overset{-}{O}$ = Calcium ox*ide*.

$\overset{+}{Ba}\overset{-}{S}$ = Barium sulph*ide*.

$\overset{+}{Zn_3}\overset{-}{P_2}$ = Zinc phosph*ide*.

Thus, compounds in which chlorine acts as the electro-negative element are called *chlorides;* with bromine, as *bromides;* with oxygen, as *oxides;* with phosphorus, as *phosphides;* and so on.

In those cases where two elements form several compounds, these are usually distinguished from one another by employing Greek numeral prefixes added to the name of the negative element. Thus,—

$\overset{III}{N_2}O$ = Nitrogen *mon*-oxide.

$\overset{III}{N_2}O_2$ = " *di*-oxide.

$\overset{III}{N_2}O_3$ = " *tri*-oxide.

$\overset{V}{N_2}O_4$ = " *tetr*-oxide.

$\overset{V}{N_2}O_5$ = " *pent*-oxide.

Frequently two elements unite to form two or more compounds. This is due to the fact that some of the acting positive elements exhibit different valencies. Thus, sulphur as a tetrad forms with oxygen sulphur di-oxide, $\overset{IV}{S}\!\!<\!\!\begin{matrix}O\\O\end{matrix}$, and as a hexad, sulphur tri-oxide, $\overset{VI}{S}\!\!<\!\!\begin{matrix}O\\O\end{matrix}\!\!=O$. Also, antimony as a triad forms with sulphur antimony tri-sulphide, $\overset{III\ II}{Sb_2S_3}\left(\begin{matrix}Sb{-}S\\ \quad S\\ Sb{-}S\end{matrix}\right)$, and as a pentad, antimony penta-sulphide, $\overset{V\ II}{Sb_2S_5}\left(\begin{matrix}Sb{=}S\\ \quad S\\ Sb{=}S\end{matrix}\right)$. In such instances other distinguishing titles may be employed in which the name of the positive atom terminates in "*ous*," indicating the lower valence, while "*ic*" indicates the higher valence. Thus,—

$\overset{IV}{SO_2}$ = Sulphur*ous* oxide (sulphur di-oxide).
$\overset{VI}{SO_3}$ = Sulphur*ic* oxide (sulphur tri-oxide).
$\overset{III}{Sb_2S_3}$ = Antimon*ous* sulphide (antimony tri-sulphide).
$\overset{V}{Sb_2S_5}$ = Antimon*ic* sulphide (antimony penta-sulphide).
$\overset{III}{P_2O_3}$ = Phosphor*ous* oxide (phosphorus tri-oxide).
$\overset{V}{P_2O_5}$ = Phosphor*ic* oxide (phosphorus pent-oxide).

Many of the above oxides are anhydrides of acids, hence may be given in addition other titles which refer to their respective acids. Thus,—

SO_2 = Sulphurous anhydride ($H_2SO_3 - H_2O = SO_2$).
SO_3 = Sulphuric " ($H_2SO_4 - H_2O = SO_3$).
P_2O_3 = Phosphorous " ($2H_3PO_3 - 3H_2O = P_2O_3$).
P_2O_5 = Phosphoric " ($2H_3PO_4 - 3H_2O = P_2O_5$).

While not being anhydrides in the strict sense of the term, the following titles refer also to their respective acids :

N_2O, Hyponitrous oxide (hyponitrous acid, HNO).
N_2O_3, Nitrous " (nitrous " HNO_2).
N_2O_5, Nitric " (nitric " HNO_3).

Nomenclature of the Acids.—The hydrogen or binary acids, being simple compounds of electro-positive hydrogen and

an electro-negative element, have the same ending as all other binary compounds,—namely, "*ide*." Thus,—

Acids.	Salts.
HCl, Hydrogen chlor*ide*.	NaCl, Sodium chlor*ide*.
HBr, " brom*ide*.	KBr, Potassium brom*ide*.
HI, " iod*ide*.	NH_4I, Ammonium iod*ide*.

Custom has followed another method, which consists in employing the term acid and preceding it by the name of the electro-negative element ending in "*ic*" with the prefix "*hydro*." The titles of the salts remain as above given.

HCl = *Hydro*chlor*ic* acid.
HBr = *Hydro*brom*ic* acid.
HI = *Hydro*iod*ic* acid.

The ternary or oxy-acids are also salts of hydrogen, hence named accordingly, the ending of the negative rest being "*ate*."

Acids.	Salts.	Acids.
HNO_3 = Hydrogen nitr*ate*.	$NaNO_3$ = Sodium nitr*ate*.	*Nitric acid.*
H_2SO_4 = " sulph*ate*.	Na_2SO_4 = " sulph*ate*.	*Sulphuric acid.*
H_3PO_4 = " phosph*ate*.	Na_3PO_4 = " phosph*ate*.	*Phosphoric acid.*

The latter titles of the acids are more customary, in which the name of the electro-negative element ending in "*ic*" is followed by the term acid.

Some elements form several oxygen acids, differing from one another in the number of molecules of oxygen present. These are distinguished from one another, when there are but two compounds, by the endings "*ous*" and "*ic*." Thus,—

Acids.	Salts.
H_2SO_3, Sulphur*ous* acid.	Na_2SO_3, Sodium sulph*ite*.
H_2SO_4, Sulphur*ic* acid.	Na_2SO_4, Sodium sulph*ate*.
HNO_2, Nitr*ous* acid.	KNO_2, Potassium nitr*ite*.
HNO_3, Nitr*ic* acid.	KNO_3, Potassium nitr*ate*.
H_3PO_3, Phosphor*ous* acid.	Na_3PO_3, Sodium phosph*ite*.
H_3PO_4, Phosphor*ic* acid.	$BiPO_4$, Bismuth phosph*ate*.

The salts of the *ic* oxygen acids terminate in "*ate*," and those of the *ous* acids in "*ite*," as shown above.

If there be more than two acids of the same elements possible, the one containing the least oxygen is designated by the prefix "*hypo*" and suffix "*ous*," the next higher compound by the suffix "*ous*," the next by the suffix "*ic*," and the

highest oxidized product by the prefix "*per*" and the suffix "*ic*." Thus,—

Acids.		Salts.	
$HClO$,	*Hypo*chlor*ous* acid.	$NaClO$, Sodium *hypo*chlor*ite*.	
$HClO_2$,	Chlor*ous* "	$NaClO_2$ "	chlor*ite*.
$HClO_3$,	Chlor*ic* "	$NaClO_3$ "	chlor*ate*.
$HClO_4$,	*Per*chlor*ic* "	$NaClO_4$ "	*per*chlor*ate*.

The following represent a number of prefixes, some of which, though antiquated, still find usage in pharmaceutical literature.

Proto means first of a series; for example, *proto*iodide of mercury (Hg_2I_2) and *proto*chloride of iron ($FeCl_2$) represent the simplest combinations of these two elements.

Deuto, *Di*, *Bin*, *or Bi.*—These prefixes refer to the number of atoms of the electro-negative element present in the compound. *Deuto-* or *bin*iodide of mercury (HgI_2), *di-* or *bi*-chloride of mercury.

Sub means below or under; thus, a *sub*oxide or *sub*chloride refers to the oxide or chloride below the normal. Since normal oxide of mercury is HgO, the suboxide would be Hg_2O $\left(\begin{matrix}Hg\\|\\Hg\end{matrix}\!\!>\!O\right)$, the latter compound containing a lower percentage of oxygen. Subchloride of mercury is $HgCl$ (or Hg_2Cl_2), and contains less chlorine than the normal or bichloride ($HgCl_2$).

Super or *Hyper* means "beyond;" thus, a *super-* or *hyper*-oxide would be the oxide beyond the normal; as, for example, normal sodium oxide is Na_2O; its next higher or superoxide is $Na_2O_2\left(\begin{matrix}Na-O\\|\\Na-O\end{matrix}\right)$. These terms are almost obsolete.

Per.—This prefix, which is frequently employed, indicates that the molecule contains the highest possible percentage of the electro-negative element or group. Thus, we have *per*chloride of iron ($FeCl_3$) as compared with *proto*chloride ($FeCl_2$); hydrogen *per*oxide would be $H_2O_2\left(\begin{matrix}O-H\\|\\O-H\end{matrix}\right)$; sodium *per*-oxide, Na_2O_2; *per*chloric acid, $HClO_4$.

Sesqui.—This term refers to a ratio of *two* atoms of the electro-positive element to *three* of the electro-negative. Thus, *sesqui*oxide of iron would be $Fe_2O_3\left(\begin{matrix}Fe=O\\>O\\Fe=O\end{matrix}\right)$; Sb_2S_3 is *sesqui*sulphide of antimony.

Stochiometry.

Stochiometry, or chemical arithmetic, is based on the fundamental laws of chemistry,—namely, Lavoisier's conservation of mass and Dalton's laws of simple and multiple proportion. Since chemical formulæ and equations are made up of symbols, and these symbols in turn represent atoms which express definite weights of matter, it is simply a question of calculation to ascertain the percentages of each element entering into the composition of a chemical compound, or the quantities of the chemicals necessary for or resulting from a chemical reaction.

Percentage Composition Calculations.—In order to ascertain the percentage of each of the elements present in the molecule of a compound, we first determine its molecular weight, then multiply the atomic weight of each of the elements by the number of atoms present, and this product by 100; this is then divided by the molecular weight of the compound. Thus, the percentage composition of sulphuric acid (H_2SO_4) would be calculated as follows:

Hydrogen (H_2) =	atomic weight	1 × 2 =	2	molecular weight.	
Sulphur (S) =	"	"	31.83 × 1 =	31.83	" "
Oxygen (O_4) =	"	"	15.88 × 4 =	63.52	" "
				97.35	" "

* Hydrogen in 100 parts would be $\frac{2 \times 100}{97.35}$ = 2.054 per cent.

Sulphur " " " $\frac{31.83 \times 100}{97.35}$ = 32.696 " "

Oxygen " " " $\frac{63.52 \times 100}{97.35}$ = $\frac{65.250}{100.000}$ " "

Molecular Formula Calculations.—Having ascertained the percentage composition and molecular weight of a compound, its molecular formula may then be calculated. For example, an analysis of a compound of nitrogen and oxygen gave

---

* This compound is made up of $\frac{2}{97.35}$ parts of H, $\frac{31.83}{97.35}$ parts of S, and $\frac{63.52}{97.35}$ parts of oxygen. In 100 parts we would have as many parts of hydrogen as

$H_2SO_4 : H_2 :: 100 : x$, of oxygen $H_2SO_4 : O_4 :: 100 : x$

$97.35 : 2 :: 100 : x$ $97.35 : 63.52 :: 100 : x$

$97.35\ x = 2 \times 100$ $97.35\ x = 63.52 \times 100$

$x = 2.054$ parts. $x = 65.250$ parts.

its percentage composition as follows : $\begin{matrix} N = 46.73- \\ O = 53.27+ \\ \hline 100.00 \end{matrix}$. Its molecular weight was 60.

To find the number of atoms of each of the elements in the molecule, we make the following proportion :

If 100 parts of the compound contain 46.73— parts of nitrogen, 60 parts contain x.

$$100 : 46.73- :: 60 : x. \qquad x = 28.038 \text{ parts.}$$

If 100 parts of the compound contain 53.27+ parts of oxygen, 60 parts contain y.

$$100 : 53.27+ :: 60 : y. \qquad y = 31.962 \text{ parts.}$$

Hence 28.038 represents the weights of the atoms of N contained in a molecule of the compound, and 31.962 the weights of the atoms of O contained in the molecule.

By dividing these numbers by the weights of the respective atoms, the number of atoms of N and O contained in the molecule is readily determined.

$$28.038 \div 13.93 = 2 \text{ atoms of nitrogen } (2.01+).*$$
$$31.962 \div 15.88 = 2 \text{ " oxygen } (2.01+).$$

Hence the formula of this compound is N_2O_2.

Equation Calculations.—This class of calculations embraces the estimation of the quantities of the various substances entering into or resulting from a chemical reaction. In such cases it is first necessary to express the complete reaction with the molecular weights of all the substances. Then make the following proportion. *As the molecular weight of the substance given in the equation is to the molecular weight of the substance required, so is the weight of the substance given in the problem to x, the weight of the substance desired.* Three terms of the equation being given, the fourth is ascertained by multiplying the two means (second and third terms) and dividing the products by the extremes (first and fourth). The first and third terms and the second and fourth must always be of the same denomination.

Problem.—How much chloride of iron (ferrous chloride) can be prepared from 100 grammes of iron?

Equation :

Fe	+	2HCl	=	$FeCl_2$	+	H_2.
55.6		72.36		125.96		2

* The nearest whole number is selected.

Statement :

$$\frac{\text{Fe (subs. given in equation)}}{55.6} : \frac{\text{FeCl}_2\text{ (subs. required)}}{125.96} :: \frac{\text{Fe (subs. given in problem)}}{100} : \frac{\text{FeCl}_2\text{ (weight of subs. desired)}}{x}.$$

$$55.6\,x = 125.96 \times 100$$
$$55.6\,x = 12596.$$
$$x = 226.5+ \text{ grammes.}$$

Therefore, 226.5+ grammes of ferrous chloride can be prepared from 100 grammes of iron.

Problem.—How many grammes of iron are necessary for the production of 100 grammes of ferrous chloride? If, according to the above equation, 55.6 parts of iron are necessary for the production of 125.96 parts of its chloride, then 43.81+ grammes of iron would be necessary for the preparation of 100 grammes of chlorides, for

$$\text{FeCl}_2 : \text{Fe} :: \text{FeCl}_2 : \text{Fe.}$$
$$125.96 \quad 55.6 \quad 100 \quad x$$
$$126.9\,x = 55.6 \times 100$$
$$x = 43.81+ \text{ grammes.}$$

Problem.—How much sodium chloride and sulphuric acid is necessary for the preparation of 1000 grammes of hydrochloric acid, U. S. P.?

Since the U. S. P. acid is an aqueous solution containing 31.9 per cent. of dry hydrochloric acid gas, in order to prepare 1000 grammes of this solution it will be necessary to pass 319 grammes of the gas through 681 grammes of water.

(31.9 per cent. of 1000 = 319. 1000 — 319 = 681.)

The question now reads, How much sodium chloride and sulphuric acid is necessary for the preparation of 319 grammes of dry hydrochloric acid gas? This gas is prepared according to the following equation :

$$\underset{\substack{\text{Sodium}\\\text{Chloride.}\\58.06}}{\text{NaCl}} + \underset{\substack{\text{Sulphuric}\\\text{Acid.}\\97.35}}{\text{H}_2\text{SO}_4} = \underset{\substack{\text{Sodium Acid}\\\text{Sulphate.}}}{\text{NaHSO}_4} + \underset{\substack{\text{Hydrochloric}\\\text{Acid Gas.}\\36.18}}{\text{HCl.}}$$

If 58.06 grammes of sodium chloride are necessary for the production of 36.18 grammes of gaseous hydrochloric acid, then for the preparation of 319 grammes of the gas 511.9+ grammes of the salt will be required, for

$$\text{HCl} : \text{NaCl} :: \text{HCl} : \text{NaCl.}$$
$$36.18 \quad 58.06 \quad 319 \quad x$$
$$36.18\,x = 58.06 \times 319$$
$$x = 511.9+ \text{ grammes of NaCl.}$$

If 97.35 grammes of sulphuric acid are necessary for the production of 36.18 grammes of gaseous hydrochloric acid, then 858.3+ grammes of the former will be necessary to prepare 319 grammes of the latter, for

$$\begin{array}{cccc} HCl : H_2SO_4 :: HCl : H_2SO_4. \\ 36.18 \quad 97.35 \quad 319 \quad x \end{array}$$

$$36.18\,x = 97.35 \times 319$$

$$x = 858.3+ \text{ grammes of } H_2SO_4.$$

Therefore, for the preparation of 1000 grammes of U. S. P. hydrochloric acid, 511.9+ grammes of sodium chloride, 858.3+ grammes of sulphuric acid, and 681 grammes of water are necessary.

Problem.—How many liters of hydrogen gas can be obtained by the action of sulphuric acid on 100 grammes of zinc?*

Equation :

$$\underset{64.9}{Zn} + H_2SO_4 = ZnSO_4 + \underset{2}{H_2}.$$

If

$$\begin{array}{cccc} Zn : H_2 :: Zn : H_2, \\ 64.9 \quad 2 \quad 100 \quad x \end{array}$$

$$64.9\,x = 2 \times 100. \qquad x = 3.081+ \text{ grammes of hydrogen.}$$

The next question that arises is to convert this 3.081+ grammes of hydrogen gas into volume liters. Since one liter of dry hydrogen (at standard temperature (0° C.) and pressure (760 millimeters) weighs 0.08995 gramme, 3.081+ grammes would measure 34.25+ liters, according to the following proportion :

$$\begin{array}{cccc} \text{Weight} : \text{volume} :: \text{weight} : \text{volume} \\ 0.08995 \text{ gramme} \quad 1 \text{ liter} \quad 3.081+ \text{ grammes} \quad x \end{array}$$

$$0.08995\,x = 3.081+ \times 1$$

$$x = 34.25+$$

Therefore, 100 grammes of zinc yield 34.25+ liters of hydrogen gas.

* It is understood that the reaction is carried on in the presence of water.

CHAPTER II.

HYDROGEN.

Symbol, H. *Atomic Weight,* 1. *Valence,* I.

History. — In the sixteenth century, Paracelsus observed hydrogen while experimenting on iron with acids. Cavendish, in 1766, first investigated it, and gave it the name "inflammable air." Lavoisier, some years later, proposed the name hydrogen, which has met with general acceptance.

Occurrence.—Hydrogen occurs, in the free state, in certain volcanic gases, in the carnallite of the Stassfurt mines, occluded in meteoric iron, and in the natural gas of the Pennsylvania oil regions. In combination, hydrogen forms one-ninth of the water of the globe, and is a constituent of nearly all organic matter.

FIG. 91.

Preparation of hydrogen by decomposition of water.

Preparation.—(1) By the decomposition of water with the electric current. An apparatus like that shown in Fig. 91 is very convenient. One part sulphuric acid to one hundred parts of water assists the process by making the latter a better conductor of electricity. The products of the action are two volumes of hydrogen and one volume of oxygen, according to the following:

$$2H_2O = 2H_2 + O_2.$$

(2) By the decomposition of water with sodium or potassium. When a small piece of potassium is thrown on water, chemical action takes place at once, the metal melts, and floats around, enveloped in a flame of hydrogen, which ignites spontaneously from the heat of the action. The flame is of a violet color, imparted by the volatilization of some of the metal.

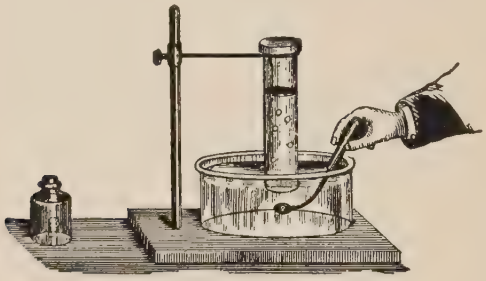
Sodium does not react so strongly with the water as to cause ignition of the escaping hydrogen, unless it be held in one spot by placing it on a piece of filter paper, when sufficient heat is developed to ignite the gas, which, in this case, burns with a

yellow flame. The metal rapidly disappears in the excess of water, forming a strongly alkaline solution :

Na_2	+	$2H_2O$	=	$2NaOH$	+	H_2.
Sodium.		Water.		Sodium Hydrate.		Hydrogen.

The gas may be collected, when sodium is used, by enclosing the metal tightly in a wire cage, and thrusting this quickly under an inverted cylinder filled with water as shown in Fig. 92.

FIG. 92.



Decomposition of water by sodium.

(3) The decomposition of water by certain metals at a red heat :

$4H_2O$	+	$3Fe$	=	Fe_3O_4	+	$4H_2$.
Water.		Iron.		Ferroso-ferric Oxide.		Hydrogen.

This reaction may be carried out by passing the vapor of water through an iron tube in which some iron wire has been placed, and the whole heated to redness ; the metal combines with the oxygen of the vapor, forming ferroso-ferric oxide, while the hydrogen passes out, and may be collected over water.

(4) By the action of dilute acids on certain metals we obtain hydrogen, as follows :

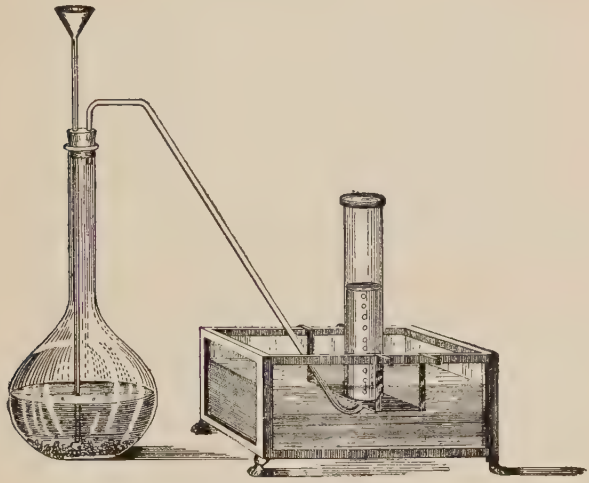
Zn	+	H_2SO_4	=	$ZnSO_4$	+	H_2.
Zinc.		Sulphuric Acid.		Zinc Sulphate.		Hydrogen.

Iron may be used in place of the zinc, or sulphuric acid may be substituted by hydrochloric acid, with similar results. Iron, however, does not yield as pure a gas as zinc, on account of certain carbon impurities contained in it.

The above reaction progresses satisfactorily only in the presence of water, which dissolves the zinc sulphate formed, and prevents its collecting on the metal and retarding the further action of the

acid. When chemically pure zinc is used the action at first is very slow, but by the addition of a drop or two of platinic chloride solution a galvanic action is established, which causes a rapid evolution of the gas. This is the method usually employed for preparing the gas for experimental purposes, and an apparatus similar to that represented in Fig. 93 will be found convenient.

FIG. 93.



Preparation of hydrogen.

The mistake is often made by beginners of attempting to ignite the gas as it escapes from the generator; this should never be done until after one has become thoroughly familiar with the properties of the element. Explosions frequently occur by neglecting this precaution.

(5) When strong solutions of the alkaline hydrates are brought in contact with certain metals, hydrogen is evolved; in some cases, like the following, it is necessary to apply heat:

$$\underset{\text{Zinc.}}{Zn} + \underset{\substack{\text{Sodium}\\\text{Hydrate.}}}{2NaOH} = \underset{\substack{\text{Sodium}\\\text{Zincate.}}}{Zn(ONa)_2} + \underset{\text{Hydrogen.}}{H_2}.$$

With magnesium and aluminum the action takes place at the ordinary temperature.

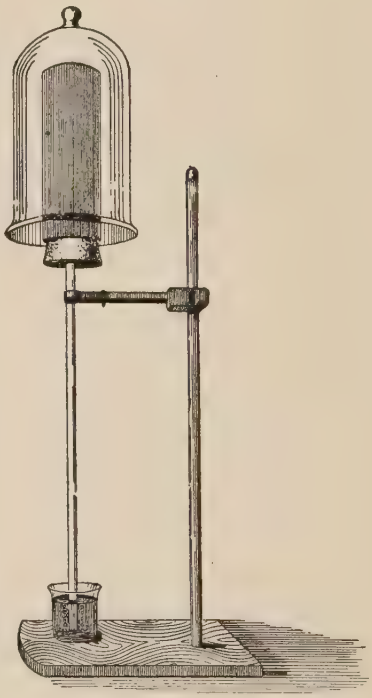
All the foregoing processes yield a gas more or less impure. In order to obtain perfectly pure hydrogen, it should be passed through a solution of lead acetate, to remove hydrogen sulphide; through a solution of silver sulphate, to remove hydrogen phos-

phide and arsenide ; through potassium hydrate solution, to remove free acid ; and, finally, over calcium oxide or phosphoric oxide, to remove moisture.

Physical Properties.—When purified as above, hydrogen is without color, odor, or taste; it is the lightest known substance ; one liter weighs 0.08995 gramme at 0° and under 760 millimeters' pressure, indicating a specific gravity of .0695 when air equals 1.000, or in the proportion of 1 to 14.42. It may, therefore, be collected by "upward displacement," by simply holding a receiver over a tube from which the gas is escaping ; this method, however, is unnecessary, as the gas is so insoluble in water that it is usually collected over that liquid.

Between the temperatures of 0° and 20°, it requires 50 volumes of water to dissolve one volume of hydrogen. Hydrogen may be inhaled for a short time without injurious effects, but it causes a peculiar change in the voice. Sound travels nearly four times more rapidly in hydrogen than in air, and light is refracted more strongly by it than by any other gas.

FIG. 94.



Diffusion of hydrogen.

The diffusibility of hydrogen is one of its most prominent characters. This property may be illustrated by an apparatus shown in Fig. 94, in which a porous battery cell securely fastened by a rubber cork on the end of a glass tube forms the diaphragm. The lower, open end of the tube is placed in water colored with aniline or indigo, and a jar full of the gas lowered around the cell, when, as the hydrogen diffuses into the cell faster than the air comes out, the latter is driven out below, and is seen bubbling up through the water ; as soon as this action ceases the jar is removed, and the hydrogen now rapidly passes out through the cell, causing a partial vacuum,

which the water rises to fill. Since the relative diffusibility of two gases is inversely as the square roots of their densities, we have (when hydrogen equals 1) $\sqrt{14.42} : \sqrt{1}$ or 3.8 : 1,—that is, hydrogen will diffuse 3.8 times more rapidly than air.

Hydrogen may be converted, by a pressure of 180 atmospheres and a temperature of —205° C., produced by the vaporization of liquid air in a vacuum, into a steel-blue liquid, and on suddenly releasing this pressure, the vaporization of the liquid is so rapid that the intense cold thus produced converts a portion of the escaping liquid into solid particles, which almost instantly disappear. The critical temperature of hydrogen gas is about 30° above absolute zero (—273° C.), while its critical pressure is only 15 atmospheres.

Hydrogen possesses the peculiar property of permeating certain metals, like iron, palladium, and platinum, at a red heat. This fact depends on the property, named by Graham *occlusion*, which some metals, especially palladium, possess, of absorbing hydrogen. For instance, platinum at 100° absorbs 0.76 volume, and at a red heat 3.8 volumes of the gas; while palladium absorbs 376 volumes at ordinary temperatures, 643 volumes at 90°, and 526 volumes at 245°. The amount absorbed depends somewhat on the physical condition of the metal, palladium deposited by electrolysis absorbing 982 volumes at 100°.

Chemical Properties.—Under ordinary conditions hydrogen has but little affinity for other substances, but at elevated temperatures or in the nascent state its behavior is quite the reverse, and we find it combines readily with oxygen; that is, burns when ignited, the product being water. The glass tube from a hydrogen generator may be converted into a jet for illustrating this property, by fusing into the end of it a small roll of platinum made from a piece of the foil. When one is sure that all the air has been expelled from the apparatus this jet may be lighted, and the gas will burn with a pale blue flame. When we ignite the gas as it issues directly from the glass tube, without using the platinum jet, the flame takes a yellow color from the sodium of the glass.

The hydrogen flame is intensely hot; in fact, its combustion indicates a higher temperature than an equal bulk of any other known substance. The temperature of the oxy-hydrogen flame, which is 2000° C., is exceeded only by the electric furnace. The great affinity of hydrogen for oxygen may be further illustrated by making a mixture of two volumes of the former to one

volume of the latter, and applying flame, when a violent explosion will occur. The same takes place when air, in larger proportion, is used instead of oxygen ; hence the importance of having all the air driven out of a generator before attempting to ignite the gas. Its affinity for most other substances is not sufficient to support their combustion when they are introduced in a burning condition into the gas. This may be illustrated by the following experiment, Fig. 95. If a cylinder of the gas is held in an inverted position, and a lighted taper or candle brought to the mouth, the gas will ignite, but on pushing the burning candle up through the flame into the pure gas, the combustion of the taper ceases, on account of the lack of affinity between its constituents and the hydrogen surrounding it. With chlorine or the other halogens hydrogen combines even more readily than with oxygen, but with most other non-metals it does not unite directly unless in the nascent state.

FIG. 95.

Hydrogen a non-supporter of combustion.

The affinity of hydrogen for the halogens decreases in proportion to their increase in atomic weight. Thus, fluorine combines with hydrogen in the dark, while chlorine requires the aid of direct sunlight ; with bromine a temperature of 200° C. and sunlight are necessary, while iodine and hydrogen combine directly with some difficulty, and the compound is quite unstable. The gaseous elements, in the moment of their formation or birth (*statu nascendi*), act more energetically than after their liberation, for the reason that this *nascent* or specially active state represents the element in its atomic condition before the atoms have united to form molecules. While in this nascent state hydrogen gas is a very active *reducing agent*,—that is, it removes a part or all of the electro-negative element of many compounds. Thus, on adding zinc or iron filings to an acid solution of the following, reduction takes place :

(1) As_2O_3 (Arsenous Oxide.) $+ 6H_2 = 2AsH_3$ (Hydrogen Arsenide.) $+ 3H_2O$.

(2) H_2SO_3 (Sulphurous Acid.) $+ 3H_2 = 3H_2O + H_2S$. (Hydrogen Sulphide.)

(3) Fe_2Cl_6 (Ferric Chloride.) $+ H_2 = 2FeCl_2$ (Ferrous Chloride.) $+ 2HCl$. (Hydrogen Chloride.)

(4) FeS (Ferrous Sulphide.) $+ H_2SO_4 = FeSO_4$ (Ferrous Sulphate.) $+ H_2S$.

In Equation 4 the acid reacts with the iron sulphide, liberating nascent hydrogen, which unites with the sulphur atom to produce hydrogen sulphide.

Hydrogen in its ordinary (molecular) state possesses reducing properties through its affinity for such electro-negative elements as oxygen, sulphur, chlorine, etc. In such cases the compound to be reduced is heated, while a current of hydrogen is passed over. Thus,—

(1) Fe_2O_3 + $3H_2$ = $3H_2O$ + Fe.
Ferric Oxide. Reduced Iron.

(2) $2CrO_3$ + $3H_2$ = Cr_2O_3 + $3H_2O$.
Chromic Peroxide. Chromic Oxide.

(3) Sb_2S_5 + $2H_2$ = $2H_2S$ + Sb_2S_3.
Antimony Pentasulphide. Antimony Trisulphide.

(4) Fe_2Cl_6 + H_2 = $2FeCl_2$ + 2HCl.
Ferric Chloride. Ferrous Chloride.

Uses.—Hydrogen has comparatively few uses in the free state. At one time, on account of its lightness, it was used for filling balloons. As a frequent constituent of natural gas and water-gas, it is useful on account of its great heating power. In the nascent state it is a valuable laboratory agent in the preparation of many chemical compounds.

PRACTICAL EXERCISES.

(1) Make hydrogen from zinc and sulphuric acid, using apparatus as arranged in Fig. 93, p. 187.

(2) Note its levity by collecting a tube full, and, holding it covered in a vertical position, bring a lighted taper a short distance above its mouth and remove the cover; the gas will rise to the flame and ignite.

(3) Another tube, similarly filled, is held in an inverted position and the cover removed; it will be found, even after the lapse of some time, that the hydrogen at the mouth of the tube may be ignited, thus demonstrating that the gas is too light to come down and out of the mouth of the tube.

(4) The two preceding experiments have demonstrated the combustibility of the gas, which, when pure, burns quietly, with a colorless flame. If, however, it be mixed with air and flame be applied, a violent explosion ensues. *Therefore the tube from the generator should never be brought near a flame until it is certain that all the air has been expelled;* this is determined by trying a test-tube full; if it burn quietly, the jet may be lighted. *This precaution should always be observed.*

(5) On bringing a lighted taper to the mouth of the inverted tube filled with hydrogen, the gas is ignited, but, on pushing the burning taper up

into the gas, its flame is extinguished ; thus showing that, while hydrogen is combustible, it is not a supporter of combustion.

(6) Continue the addition of acid to the zinc until the latter is nearly all dissolved ; disconnect the apparatus, pour the liquid on a filter, collect the filtrate in a small beaker or evaporating dish, concentrate by heat, and set aside for twenty-four hours to crystallize. The crystals obtained are *zinc sulphate*, $ZnSO_4$, the result of a combination of the sulphuric acid and the zinc, as follows :

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

CHAPTER III.

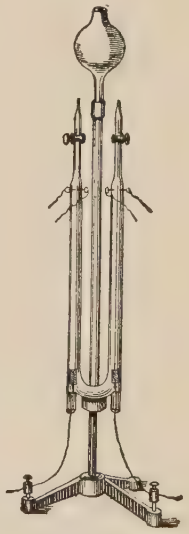
THE HALOGENS.

CHLORINE.

Symbol, Cl. *Atomic Weight*, 35.18. *Valence*, I.

History.—Chlorine was first prepared by Scheele, in 1774, while experimenting with "black magnesia" (an ore consisting largely of manganese dioxide) and hydrochloric acid, but its elementary character was first established by Davy, in 1801, who gave to it the name of chlorine on account of its greenish-yellow color.

FIG. 96.



Decomposition of hydrochloric acid by electrolysis.

Occurrence.—Chlorine does not occur in the free state in nature, but is found abundantly in combination with sodium, in sea water, and in the salt-wells of the United States; also as rock-salt in the mines of Austria, Spain, and Bavaria, all of which have been worked for centuries. It is also found in certain "horn" minerals, combined with lead, silver, or mercury.

In the vegetable kingdom chlorine is not very abundant, but in the animal kingdom, combined with sodium, it is found more abundantly, being a constituent of most animal secretions.

Preparation.—Chlorine may be prepared by a number of different processes, as follows:

(1) By the electrolysis of hydrochloric acid or of chlorides. The decomposition of the former is readily carried out in an apparatus shown in Fig. 96.

(2) By the decomposition of certain chlorides by heat, those of gold, palladium, and platinum giving up the gas most readily.

$$\underset{\text{Platinic Chloride.}}{PtCl_4} = \underset{\text{Platinous Chloride.}}{PtCl_2} + \underset{\text{Chlorine.}}{Cl_2}.$$

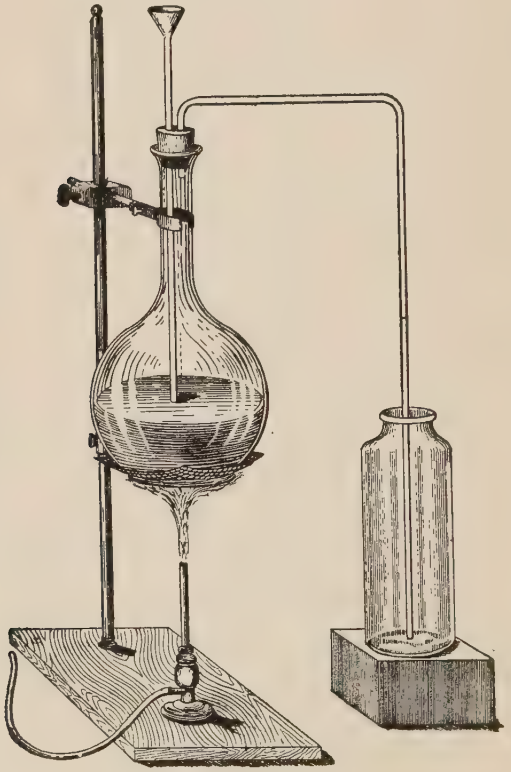
(3) On heating a mixture of manganese dioxide and hydrochloric acid, chlorine is given off abundantly, and may be col-

lected over warm water, or by "downward displacement," as illustrated in Fig. 97. The reaction which takes place may be expressed as follows:

$$\underset{\text{Manganese Dioxide.}}{MnO_2} + \underset{\text{Hydrochloric Acid.}}{4HCl} = \underset{\text{Manganous Chloride.}}{MnCl_2} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Chlorine.}}{Cl_2}.$$

This is the method of the U. S. Pharmacopœia. Care should be taken to mix the acid thoroughly with the powder, to prevent any of the latter from remaining unmoistened on the bottom and

FIG. 97.



Preparation of chlorine.

causing fracture of the flask on the application of heat. The oxide should be in excess of the acid, and heat should not be applied for some minutes after they are mixed, or the resulting gas will be mixed with hydrochloric acid. As an additional pre-

caution it has been recommended to use the oxide in lumps, and have them above the surface of the acid; even then the gas should be passed through a small quantity of water, to remove the last traces of acid, before collecting it in the receiver.

(4) By mixing in an apparatus similar to that used in the preceding process, five parts of manganese dioxide, four parts of sodium chloride, and a mixture of twelve parts of sulphuric acid with six parts of water:

$$\underset{\text{Manganese Dioxide.}}{MnO_2} + \underset{\text{Sodium Chloride.}}{2NaCl} + \underset{\text{Sulphuric Acid.}}{2H_2SO_4} = \underset{\text{Manganous Sulphate.}}{MnSO_4} + \underset{\text{Sodium Sulphate.}}{Na_2SO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Chlorine.}}{Cl_2}.$$

This process has been recommended on the score of economy; but in these days of cheap hydrochloric acid this cannot be urged as a perceptible advantage over the preceding.

(5) Most peroxides and other oxidizing agents cause an evolution of chlorine when heated with hydrochloric acid, provided the corresponding chloride does not exist or is unstable. With potassium dichromate the reaction is as follows:

$$\underset{\text{Potassium Dichromate.}}{K_2Cr_2O_7} + \underset{\text{Hydrochloric Acid.}}{14HCl} = \underset{\text{Chromic Chloride.}}{Cr_2Cl_6} + \underset{\text{Potassium Chloride.}}{2KCl} + \underset{\text{Water.}}{7H_2O} + \underset{\text{Chlorine.}}{3Cl_2}.$$

(6) As a rapid method in the laboratory, hydrochloric or sulphuric acid added to bleaching powder will give an abundance of the gas:

$$\underset{\text{Bleaching Powder.}}{Ca(ClO)_2.CaCl_2} + \underset{\text{Hydrochloric Acid.}}{4HCl} = \underset{\text{Calcium Chloride.}}{2CaCl_2} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Chlorine.}}{2Cl_2}.$$

This process is extensively used in bleaching and disinfecting operations.

(7) The process of Deacon, in which the hydrochloric acid from the Leblanc soda process is passed, with air, over pieces of brick saturated with cupric and sodium sulphates, and heated to about 500° to 700°, has been used largely in England for the preparation of chlorine to be used in the manufacture of bleaching powder. The exact chemical action of the salts of sodium and copper is not well understood, except that they enable the following reaction between the hydrochloric acid and the oxygen of the air to take place at a lower temperature than would the bricks alone:

$$4HCl + O_2 = 2H_2O + 2Cl_2.$$

This chlorine is mixed with some undecomposed hydrochloric acid and the nitrogen of the air, but is, nevertheless, adapted to the purposes for which it is used. Cuprous chloride has been employed in the place of cupric sulphate with somewhat better results; in fact, it has been shown that a number of substances bring about the action, notably magnesium oxide.*

(8) The method of Weldon has been used for the same purpose. This, however, is a modification of the decomposition of hydrochloric acid by manganese dioxide, adapted to an industrial scale, by which the latter compound is recovered and used for decomposing fresh quantities of hydrochloric acid indefinitely.

This process consists in decomposing magnesium oxychloride by passing air over it at a temperature of 1000°. The magnesium salt is converted into oxide, while the chlorine, mixed with nitrogen and small quantities of hydrochloric acid, is passed through a purifying system, and then over lime, which it converts into bleaching powder. The magnesium oxychloride is prepared by dissolving magnesium oxide in the hydrochloric acid of the Leblanc process, or from the ammonium chloride of the ammonia-soda process. In both cases it utilizes what would otherwise be a waste product, it being possible to use the same magnesia indefinitely. The reaction which takes place may be considered a decomposition of magnesium chloride, since the oxychloride is made by mixing the oxide with the chloride:

$2MgCl_2$	+	O_2	=	$2MgO$	+	$2Cl_2$.
Magnesium Chloride.		Oxygen.		Magnesium Oxide.		Chlorine.

It is claimed for the Weldon-Pechiny process that 72 per cent. of the hydrochloric acid can be recovered as chlorine, and more recently, by combination of this with the potassium chlorate process of Muspratt and Eschellmann, it is possible to recover 90 per cent. of the acid employed. As an objection to this and the preceding process, it is urged that the chlorine is diluted with nitrogen and air, to such an extent that it cannot be used in the preparation of bleaching powder. This is, however, contrary to the claims of the inventors.

(9) For a number of years the decomposition of sodium chloride by electrolysis with production of chlorine and sodium hydrate has claimed the attention of chemists, and there are at present three forms of this method in operation. When anodes

* Journal of the Society of Chemical Industry, 1888, p. 286.

and cathodes are placed opposite each other in a solution of sodium chloride, but without being separated by a porous diaphragm, the electric current gives rise to the formation of hypochlorite of sodium. But if porous diaphragms are placed between the positive and negative plates in such a way as to form water-tight compartments, chlorine will be generated in all the positive compartments and sodium in all the negative ones. The reaction is as follows :

$$\underset{\text{Sodium Chloride.}}{2NaCl} = \underset{\text{Sodium.}}{Na_2} + \underset{\text{Chlorine.}}{Cl_2.}$$

The chlorine is used in making bleaching powder ; the sodium reacts with the water present and forms sodium hydrate. For a more detailed explanation, see "Castner Process," p. 869.

Physical Properties.—Chlorine is a yellowish-green gas, of a suffocating odor and an astringent taste. It is 2.45 times heavier than air, hence may readily be collected by displacement. Under a pressure of six atmospheres at 0°, or at —34° under ordinary pressure, it is converted into a yellow liquid, which has a specific gravity of 1.38, boils at —33.6°, and solidifies at —102°. Chlorine is now commercially supplied as a compressed liquid in steel cylinders. Water at 10° is the best for dissolving chlorine, as at that temperature one volume takes up 2.58 volumes of the gas ; below that temperature a crystalline compound, $Cl_2.10H_2O$, commences to separate out. These crystals may be dried between filter paper, and preserved in a sealed tube, where they do not decompose until a temperature of 3.8° is reached. If, however, they be exposed to the air, decomposition soon commences.

Chemical Properties.—Chlorine combines readily with hydrogen on the application of flame, or when exposed to the direct rays of the sun, forming hydrochloric acid. For oxygen it has very slight affinity, as it will not burn in air, or support ordinary combustion, unless it be that of a substance rich in hydrogen, like the wax or paraffin of a taper. This affinity for hydrogen is illustrated in its behavior toward a number of compounds. If a piece of filter paper be moistened with warm turpentine oil and plunged into a jar of chlorine, the oil bursts into flame, at the same time there is a copious evolution of black smoke from the liberated carbon. Marsh gas, CH_4, or olefiant gas, C_2H_4, mixed with chlorine, will burn on the application of flame, with abun-

dant deposition of carbon. Phosphorus, antimony, copper, and a few other metals inflame when finely divided and poured into a jar of chlorine. On account of its affinity for hydrogen, chlorine is a powerful oxidizer, and for this reason is largely used as a bleaching and disinfecting agent. The reaction which takes place when chlorine bleaches organic matter in the presence of moisture, is first its combination with hydrogen, which liberates oxygen, and second the combination of this oxygen, in the nascent state, with the elements of the coloring matter, forming colorless compounds. When used for disinfecting, the compound known as *bleaching powder* or *chlorinated lime* is usually employed, either alone or mixed with diluted hydrochloric acid or vinegar. Moisture is necessary in order to obtain good results in either bleaching or disinfecting, since perfectly dry chlorine does not bleach. It is also well to remember that only the organic colors are affected by chlorine; for this reason printing ink is not destroyed, on account of its containing lamp-black or carbon, while written characters are at once decolorized. Under the name of **aqua chlori**, U.S.P., the solution of the gas is official. The U.S. Pharmacopœia requires that the solution contain "at least 0.4 per cent. of the gas." Chlorine water is a transparent greenish-yellow liquid, with a specific gravity of 1.003. It should be preserved in well-stoppered bottles, protected from the light, as it decomposes into hydrochloric acid and oxygen according to the following reaction:

$$2Cl_2 + 2H_2O = 4HCl + O_2.$$

In addition to its use in medicine as a stimulant and antiseptic, chlorine water is a valuable laboratory reagent, being especially employed for liberating iodine and bromine from combination, and for oxidizing many metallic compounds.

PRACTICAL EXERCISES.

(1) Make chlorine from manganese dioxide and hydrochloric acid, as shown in Fig. 97, p. 194.

(2) Pass the gas into water; it is absorbed; if this be continued until the water is saturated, it will be found to have absorbed about twice its volume of the gas; the chlorine water, **aqua chlori**, of the Pharmacopœia is the resulting product.

(3) A tube full of the gas, held with mouth upward and a lighted taper applied, fails to ignite, indicating that the gas is not combustible. Push the lighted taper into the gas; it is extinguished, or only burns with a small, dense, smoky flame, the result of a combination of the chlorine with the hydrogen of the material composing the taper, whereby carbon is liberated.

(4) Into a tube full of the gas put a piece of brightly dyed calico or blue litmus paper, previously moistened; it is rapidly bleached. Written characters on paper are similarly decolorized, but printed characters are not affected, as the latter contain carbon, in the form of lamp-black, which is not acted on by the gas.

HYDROGEN AND CHLORINE.

HYDROCHLORIC ACID.

Formula, HCl. *Molecular Weight,* 36.18.

History.—Hydrochloric acid in solution was known to the ancients, the alchemists being familiar with *aqua regia*, obtained by distilling nitre, sal ammoniac, and vitriol together. Glauber, about the year 1648, first prepared the aqueous acid, and gave it the name of *spiritus salis*, which as "spirits of salt" it retains to the present day. Priestley first collected the gas by the use of a pneumatic trough containing mercury. Davy, in 1810, disproved its supposed elementary character, and demonstrated it to be a compound of chlorine and hydrogen.

Occurrence.—Hydrochloric acid occurs uncombined in the gases from certain volcanoes, and in the rivers of South America which originate in the volcanic regions of the Andes.

Preparation.—When equal volumes of chlorine and hydrogen are mixed and exposed to diffused daylight, they slowly combine, forming hydrochloric acid, which may easily be shown to possess properties entirely different from either of its constituents. This combination may be effected at once and with explosion by exposing the mixture to the direct rays of the sun, to the light of the electric arc, to burning magnesium, or by the application of flame. For laboratory purposes the gas may be prepared in a flask with suitable attachments for washing and purifying, as in Fig. 98, by adding to sodium chloride one and a half times its weight of sulphuric acid, previously diluted with half its weight of water, and applying heat. A small quantity of sulphuric acid is put in the wash bottle to remove moisture, and the gas is then collected over mercury. When two molecules of sodium chloride (116.74 parts) and one molecule of the acid (97.82 parts) are taken the following reaction occurs:

$2NaCl$	$+$	H_2SO_4	$=$	Na_2SO_4	$+$	$2HCl.$
Sodium Chloride.		Sulphuric Acid.		Sodium Sulphate.		Hydrochloric Acid.

In working on a small scale, however, it is better to use the

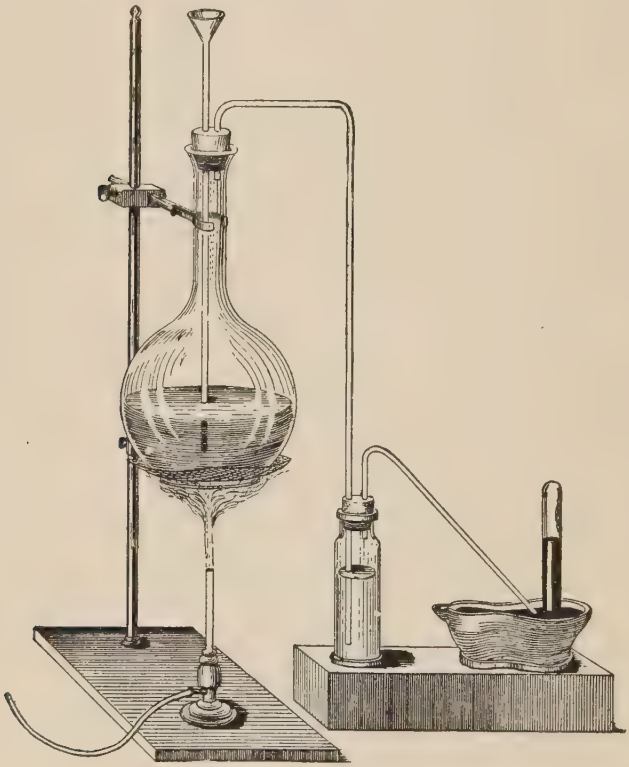
proportion of one molecule of each, when a more soluble acid sodium sulphate remains in the flask :

$NaCl$	$+$	H_2SO_4	$=$	$NaHSO_4$	$+$	HCl
Sodium Chloride.		Sulphuric Acid.		Acid Sodium Sulphate.		Hydrochloric Acid.

This reaction occurs with the aid of less heat than is required in the first, and is in other ways more satisfactory.

Properties.—Hydrochloric acid is a colorless gas, of a sharp, suffocating odor and an acid taste. It has a specific gravity, compared with air, of 1.261, and may therefore be collected like chlorine by downward displacement. It has been liquefied by a

FIG. 98.



Preparation of hydrochloric acid.

pressure of 40 atmospheres and a temperature of 10°, or of 2 atmospheres at —70° ; its critical temperature is 52.3° and critical pressure 86 atmospheres. In the liquid state it has a

specific gravity of 0.908 at 0°, and boils at —80.3°. As a liquid it has but feeble solvent action on most substances, aluminum alone, among the metals, being attacked by it. The gas is very soluble in water; at 0° one volume of water will absorb about 503 volumes of the gas. It is neither combustible nor a supporter of combustion, unless it be of metallic sodium, potassium, or magnesium, in which case hydrogen is evolved and a chloride of the metal formed. Certain oxides may be decomposed by the gas, with the formation of water and a chloride. Thus,—

$$\underset{\text{Ferric Oxide.}}{Fe_2O_3} + 6HCl = \underset{\text{Ferric Chloride.}}{Fe_2Cl_6} + 3H_2O.$$

With superoxides the products of reaction vary. For example, the superoxides of the alkalies or alkali earth yield hydrogen peroxide in cold solution,—

$$\underset{\text{Barium Superoxide.}}{BaO_2} + 2HCl = BaCl_2 + H_2O_2,$$

while lead or manganese peroxide yields a perchloride, $MnO_2 + 4HCl = MnCl_4 + 2H_2O$, which, on heating, decomposes into chlorine and the normal chloride, $MnCl_4 = MnCl_2 + Cl_2$.

Acidum Hydrochloricum, U.S.P.—This and the muriatic or hydrochloric acid of commerce are aqueous solutions of the gas in water. The official acid has a specific gravity of 1.163, and contains 31.9 per cent. of the gas. The commercial acid is a by-product in the Leblanc soda process, in which the gas is produced from salt and sulphuric acid, according to the reactions above given, but the method of dissolving the gas is different.

The decomposition of the salt is carried out in what is known as a salt-cake furnace, as shown in Fig. 99. It consists of two important parts,—namely, the pan, E, in which the sulphuric acid and salt are mixed and heated, and the muffle, B, in which the mixture is further heated at a higher temperature in order to complete the decomposition and drive off the remainder of the hydrochloric acid gas.

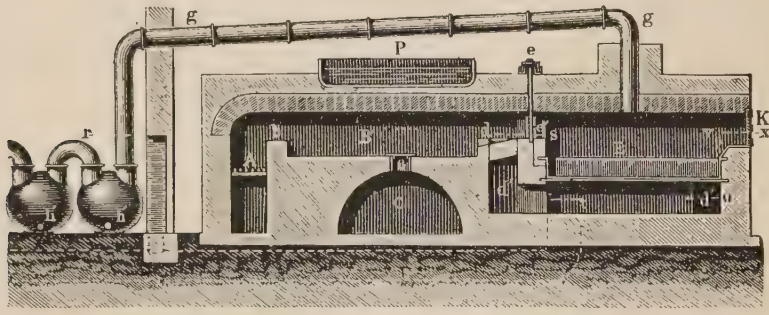
This gas is then forced through the pipe, *g g*, into the stoneware vessels, *h' h'*, or else through a system of tall towers in which are coke or bricks, and over these a constant stream of water trickles, carrying down with it the absorbed gas, until, when the bottom is reached, a strong, nearly saturated solution is the result.

This solution is then run off into suitable receivers. Such a

tower is shown in Fig. 100. There are rarely less than two of them associated with each salt-cake furnace, and the gas which escapes condensation in the first one is conveyed to the bottom of the second and forced up through it.

The acid thus prepared is of a pale-yellow color, due to small quantities of ferric chloride, organic matter, and other impurities difficult to remove. When the pure acid is desired it is necessary to make it in glass vessels from pure materials. The pure acid is colorless, of a pungent odor, and a very sour taste. It fumes strongly when exposed to the air, and gives off hydrochloric acid gas when heated, until the solution is reduced to a

FIG. 99.



Commercial preparation of hydrochloric acid.

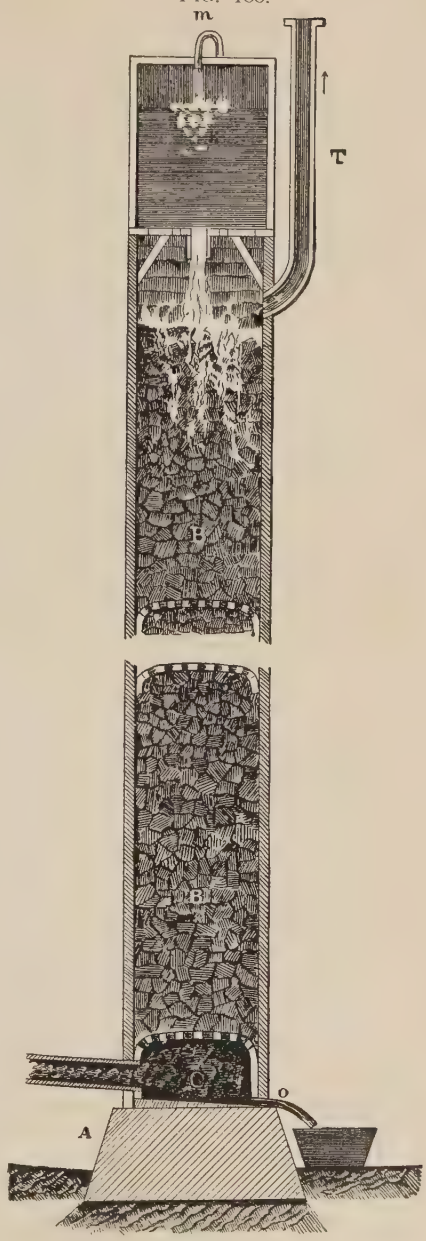
strength, under ordinary pressure, of 20.24 per cent., when it distils unchanged at 110°. When a weak acid is heated, water distils over until the solution reaches the strength of 20.24 per cent., when it distils unchanged.

Hydrochloric acid possesses the chemical properties of an energetic acid. It decomposes carbonates, phosphates, and most other salts, and dissolves nearly all the metals. Its action is without the oxidizing effect which usually accompanies nitric acid.

Impurities.—Hydrochloric acid is not often adulterated, but may contain impurities acquired in its manufacture or from carelessness in handling. It should leave no residue on evaporation to dryness, showing the absence of saline impurities and organic matter. On diluting with four volumes of water, and saturating with hydrogen sulphide, no precipitate or coloring should occur, indicating freedom from lead, arsenic, tin, thallium, and copper; nor should it acquire a blue color with ammonia in excess (cop-

per). Potassium sulphocyanate should not cause a red color (iron). A cold, dilute solution of starch and potassium iodide should not give a blue color (chlorine). When the acid is diluted with two volumes of water and placed in a test-tube with a small piece of zinc, no color should be imparted to a loose plug of cotton moistened with lead acetate solution and placed in the upper part of the tube (sulphurous acid), nor to a piece of filter paper moistened with one drop of silver nitrate solution and placed above the cotton (arsenic). When diluted with ten volumes of water, no precipitate should occur on the addition of a few drops of barium chloride solution (sulphates). The presence of free chlorine may indicate that nitric or nitrous acid is present. This may definitely be determined by adding a piece of gold-leaf, warming for some minutes, and then testing the solution with stannous chloride for gold, or by adding sodium hydrate to the original acid until strongly alkaline, and heating with pure zinc, when, if nitric

FIG. 100.



Coke tower.

or nitrous acid be present, ammonia will be evolved, and may be detected by holding a piece of moistened red litmus paper in the mouth of the tube.

Chlorides.—The compounds of hydrochloric acid are known as chlorides, and they are usually formed by dissolving the metal, a hydrate, or carbonate in the acid. A few are made by the direct action of chlorine on the metal. Nearly all metallic chlorides are soluble in water, the exceptions being the chlorides of silver, mercury (ous), and lead, the last of which is soluble in hot water.

Tests.—Hydrochloric acid and chlorides are detected by the insoluble white precipitates formed with silver, mercurous, or lead nitrates. The first forms silver chloride, AgCl, soluble in ammonium hydrate, the second mercurous chloride, Hg_2Cl_2 (calomel), which blackens on the addition of ammonium hydrate, and the third lead chloride, $PbCl_2$, which is soluble in hot water.

Uses.—Both hydrochloric acid and the chlorides are extensively used in medicine and the arts. There is scarcely an industry in which hydrochloric acid is not largely consumed. The greatest production of it is as a by-product in the soda industry, from which it goes to be converted into chlorine to furnish bleaching powder.

PRACTICAL EXERCISES.

(1) Make hydrochloric acid by taking one test-tube full of hydrogen and another of chlorine, bring their mouths together (the hydrogen tube above with mouth down, as it is lighter), turn over once or twice, so as to thoroughly mix, and open their mouths to a flame; a sharp report will occur, with the development of strongly acid fumes, which may be recognized by silver nitrate as *hydrochloric acid.*

(2) Prepare a quantity of hydrochloric acid gas, using the same or similar apparatus to that employed in the preparation of chlorine. Place some sodium chloride (common salt) in the flask and slowly add sulphuric acid; when the evolution of gas ceases, apply a gentle heat. The gas, being heavier than air, may be collected by placing the delivery-tube in a jar or test-tube. When it is desired to have the gas pure, it should be dried by passing through sulphuric acid, and then collecting over mercury.

(3) Fill a dry test-tube, or jar, with the gas, cover, and, having inverted the vessel and brought its mouth under water, remove the cover; the water so readily absorbs the gas that it rises and nearly fills the vessel. More of the solution may be made by passing the gas into water. The resulting solution, when of proper strength, is the **acidum hydrochloricum** of the Pharmacopœia.

(4) A piece of moistened blue litmus paper is instantly reddened when held in a tube of the gas, indicating its acid nature.

(5) A lighted taper applied to the gas fails to ignite it, and is extinguished if lowered into it, thus showing that the gas is neither combustible nor a supporter of combustion.

(6) Bring a rod moistened with ammonia water over the mouth of a tube full of the gas; dense white fumes of ammonium chloride are formed.

(7) Dissolve the mixture remaining in the flask, after the hydrochloric acid gas has been prepared, in warm water, add sodium carbonate so long as active effervescence ensues, whereby the excess of sulphuric acid is neutralized. The solution, when filtered, concentrated, and set aside, yields crystals of *sodium sulphate* (Glauber salt).

BROMINE.

Symbol, Br. *Atomic Weight*, 79.34. *Valence*, I.

History.—This element was discovered in 1826 by Balard, of Montpellier, France, in the bittern from the manufacture of salt on the Mediterranean.

Occurrence.—Bromine occurs chiefly as magnesium bromide in sea water, and as the magnesium, calcium, or sodium salt in many rock-salt deposits and salt-wells. Large quantities of bromine are produced at Stassfurt, a considerable quantity is manufactured from the residues after the preparation of iodine from kelp, but the greatest portion of the world's supply comes from the salt-wells of the United States.

The first production of bromine in this country was at Freeport, in Pennsylvania, in 1846; but it was not until 1866, when bromides came into use in medicine, that the industry assumed significant proportions. In 1871 shipments commenced to Europe, and in 1891 the production amounted to 415,000 pounds, divided as follows: Pennsylvania, 140,000 pounds; West Virginia, 120,000 pounds; Ohio, 110,000 pounds; and Michigan, 45,000 pounds. The production for 1899 was 433.003 pounds, which includes that in the crude bromides.

Bromine has also been found in certain cruciferous plants, and in many marine plants and animals, but it does not naturally occur anywhere in the free state.

Preparation.—The bittern, which is the mother liquor from the crystallization of salt, is concentrated to about 45° B., which causes the separation of the more insoluble sulphates and chlorides, and then manganese dioxide and sulphuric acid are added, which liberate the bromine, according to the following reaction:

$$\underset{\text{Magnesium Bromide.}}{MgBr_2} + \underset{\text{Manganese Dioxide.}}{MnO_2} + \underset{\text{Sulphuric Acid.}}{2H_2SO_4} = \underset{\text{Magnesium Sulphate.}}{MgSO_4} + \underset{\text{Manganous Sulphate.}}{MnSO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Bromine.}}{Br_2}.$$

The application of heat completes the reaction. The vapors are conducted through a condensing apparatus into well-cooled receivers. The bromine is afterward purified from water by distillation over calcium chloride, and from chlorine by distilling with a bromide (KBr or $FeBr_2$), which liberates bromine and forms a chloride :

$$\underset{\text{Potassium Bromide.}}{2KBr} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Potassium Chloride.}}{2KCl} + \underset{\text{Bromine.}}{Br_2}.$$

Another method, used on a large scale at Stassfurt, is the continuous process of decomposing the bromides by a current of chlorine and steam. The liquor flows into the top vessel of a series, arranged in a terrace, while the chlorine passes into the lowest vessel, meeting the nearly-exhausted bromide liquor. The bromine passes out of the highest vessel and is condensed by suitable means.

Properties.—Bromine is a dark, reddish-brown, volatile liquid, of a suffocating odor and a caustic taste. When exposed to the air orange-red vapors are constantly evolved, which strongly attack the eyes. The name, from *βρωμος*, stench, was given it on account of its disagreeable odor. Its specific gravity at 15° is 2.99. Pure bromine boils at 58.7°, and when cooled solidifies to brown-gray, crystalline scales, like iodine, which melt at —7.05°.

Bromine is soluble in thirty parts of water at 15°, and readily soluble in alcohol, ether, chloroform, and carbon disulphide, the last three being capable of extracting it from its aqueous solution on agitation. It is also soluble in solution of potassium or sodium bromide and in hydrobromic acid. The saturated solution in water is of a reddish-brown color, and contains at 15° one part bromine in twenty-nine parts of water. At —2° a crystalline hydrate, $Br_2.10H_2O$, separates, which decomposes at 6.2°.

In chemical properties bromine closely resembles chlorine, although it usually acts with less energy. It is not combustible, nor will it support ordinary combustion, unless it be that of a jet of burning hydrogen lowered into its vapor. With many metals it combines directly, forming bromides, a notable example being potassium, with which it combines with explosive violence ; but with sodium the union is extremely slow, it being possible to

boil the two together without causing perceptible action. Bromine possesses the property of bleaching organic compounds, but in a less degree than chlorine. It bleaches litmus and indigo solutions and colors solution of starch yellow.

Impurities and Tests.—Bromine should vaporize completely without residue. If three grammes of bromine be mixed with 30 c.c. of water, and enough ammonia water added to render the solution colorless, the liquid then digested with barium carbonate, filtered, evaporated to dryness, and the residue gently ignited, the latter should be soluble in absolute alcohol without leaving more than 0.26 gramme of residue, indicating the absence of more than 3 per cent. of chlorine. This test is founded on the fact that barium bromide is soluble and barium chloride insoluble in absolute alcohol.

If an aqueous solution of bromine be poured upon reduced iron, and shaken with the latter until nearly colorless, then filtered, mixed with gelatinized starch, and a few drops of bromine water be carefully poured on top, not more than a very faint blue zone should appear at the line of contact of the two liquids; such a blue zone would indicate iodine.

Uses.—In the free state bromine is used in the manufacture of bromides and of many bromine derivatives of the coal-tar compounds. It has also been used in medicine, internally, when largely diluted, as an alterative, like iodine, and externally as a caustic and for dissolving gangrene. It is also extensively used as a disinfectant. After the Johnstown flood in Pennsylvania, in 1889, over six thousand pounds were used for disinfecting purposes.

PRACTICAL EXERCISES.

(1) Pass chlorine into a dilute (about 1 per cent.) solution of potassium bromide; the liquid will become reddish-brown in color, owing to separation of bromine, which remains dissolved in the water.

(2) To a portion of the liquid resulting from the above experiment add a solution of starch; a yellow color will be developed, due to the formation of a compound of starch with bromine.

(3) To the remainder of the solution in a test-tube add a few drops of chloroform and agitate; the chloroform will remove the bromine from the water, and will settle to the bottom of the tube as a deep, reddish-brown liquid, while the water above will become nearly colorless.

(4) Place a little bromine in a capsule and cover it with a stoppered bell jar. Take out the stopper and drop a fragment of metallic potassium upon the bromine. A loud explosion will follow.

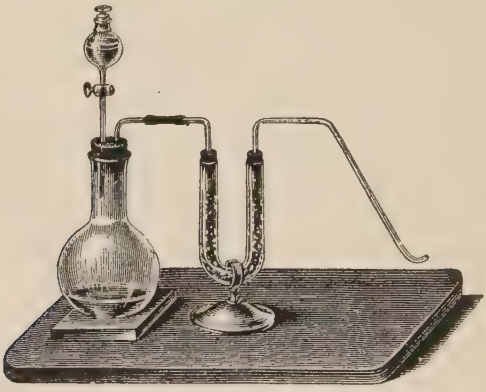
BROMINE AND HYDROGEN.

HYDROGEN BROMIDE.

Formula, HBr. *Molecular Weight,* 80.34.

Preparation.—When equal volumes of hydrogen and bromine vapor are mixed, they do not explode by the application of flame as in the case of hydrogen and chlorine, but when the mixture is passed over red-hot platinized asbestos, combination takes place and hydrogen bromide or hydrobromic acid gas results. The same compound is formed when a jet of hydrogen is burned in bromine vapor. A more practical method is to take one part of amorphous phosphorus, mix it with two parts of water, in a flask to which is fitted, with a good cork, a stoppered funnel tube containing ten parts of bromine. The apparatus may be arranged as in Fig. 101.

FIG. 101.



Preparation of hydrobromic acid.

The stop-cock is opened so as to allow the bromine to run in drop by drop, when the following reactions take place:

$$\underset{\text{Phosphorus.}}{P_4} + \underset{\text{Bromine.}}{10Br_2} = \underset{\substack{\text{Phosphorus}\\\text{Pentabromide.}}}{4PBr_5}.$$

$$\underset{\substack{\text{Phosphorus}\\\text{Pentabromide.}}}{PBr_5} + \underset{\text{Water.}}{4H_2O} = \underset{\substack{\text{Hydrogen}\\\text{Bromide.}}}{5HBr} + \underset{\substack{\text{Phosphoric}\\\text{Acid.}}}{H_3PO_4}.$$

The action is somewhat violent at first, and great care should be exercised during the operation to thoroughly agitate the mixture in order to bring the two elements in contact, and pre-

vent the collection in one place of any appreciable quantity of bromine. The escape of any free bromine is prevented by connecting the flask with a tube containing amorphous phosphorus mixed with pieces of glass. By this means the hydrogen bromide formed in the flask is augmented by that formed in the tube. After the first action ceases it is necessary to apply a gentle heat, when the gas comes off freely, and is best collected by downward displacement. Hydrobromic acid attacks mercury somewhat, so it is not a suitable medium over which to collect it, as was the case with hydrochloric acid.

By heating together potassium bromide and phosphoric acid the gas is evolved as follows :

$$\underset{\text{Potassium Bromide.}}{3KBr} + \underset{\text{Phosphoric Acid.}}{H_3PO_4} = \underset{\text{Potassium Phosphate.}}{K_3PO_4} + \underset{\text{Hydrobromic Acid.}}{3HBr.}$$

It naturally occurs to one that a cheaper acid, like sulphuric, might be substituted ; this, however, cannot be done in the case of the gas, but only in the preparation of the aqueous solution, since in the concentrated solution a decomposition takes place as follows :

$$\underset{\text{Potassium Bromide.}}{2KBr} + \underset{\text{Sulphuric Acid.}}{3H_2SO_4} = \underset{\text{Acid Potassium Sulphate.}}{2KHSO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Sulphur Dioxide.}}{SO_2} + \underset{\text{Bromine.}}{Br_2.}$$

Hydrobromic acid gas is a by-product in the preparation of many organic bromides. Thus,—

$$\underset{\text{Camphor.}}{C_{10}H_{16}O} + 2Br = \underset{\text{Monobromo-camphor.}}{C_{10}H_{15}BrO} + HBr.$$

$$\underset{\text{Benzene.}}{C_6H_6} + 2Br_2 = \underset{\text{Dibrom-benzene.}}{C_6H_4Br_2} + 2HBr.$$

Properties.—Hydrogen bromide is a colorless, heavy gas, with a sharp, irritating odor and an acid taste and reaction. At a temperature of —73° it becomes a colorless liquid, which, by a further reduction of temperature to —87°, forms a nice-like solid. The gas has a specific gravity of 2.8 (air = 1), and is very soluble in water. It is neither combustible nor a supporter of combustion. Chlorine readily decomposes hydrogen bromide according to the following reaction :

$$2HBr + Cl_2 = 2HCl + Br_2.$$

Many metals react with hydrogen bromide, forming bromides.

Acidum Hydrobromicum Dilutum, U. S. P.—As stated

above, the gas is very soluble in water, and on account of its use in medicine this solution is worthy of especial consideration. Water saturated with the gas at 0° furnishes a solution which fumes strongly on exposure to the air, and has a specific gravity of 1.78. According to Biel, that of 50 per cent. strength has a specific gravity of 1.513 at 15°.

The official acid contains 10 per cent. of hydrobromic acid gas, and has a specific gravity, according to the Pharmacopœia, of about 1.077, which, as pointed out by Dr. Squibb, should be 1.0698. On the application of heat the strong acid gives off gas until the strength is reduced to 48 per cent., when it distils unchanged at a temperature between 125° and 126°, and possesses a specific gravity of 1.49 at 15°. When a weaker acid is heated, water distils over until the contents of the still reach the above strength, when it passes over unchanged. Like hydrochloric acid, the strength of the distillate varies according to the pressure.

An acid of 34 per cent. strength may be prepared by Dr. Squibb's method,* and then diluted to a 10 per cent. strength.

An acid of 48 per cent. strength may be prepared as follows: One hundred grammes of coarsely-powdered potassium bromide and 150 c.c. of sulphuric acid, specific gravity 1.41, are moderately warmed until solution is effected, and then distilled. Boiling commences at 126°, and the temperature slowly rises to 150°. During this time most of the hydrobromic acid distils over. Traces of sulphuric acid are carried over with the last portions of the distillate, and if the bromide contain bromate the first portions of the distillate will contain bromine.

A method frequently used when a dilute acid is desired consists in passing hydrogen sulphide into an aqueous solution of bromine containing some undissolved bromine. The reaction takes place as follows:

$$\underset{\text{Bromine.}}{Br_2} + \underset{\substack{\text{Hydrogen}\\\text{Sulphide.}}}{H_2S} = \underset{\substack{\text{Hydrogen}\\\text{Bromide.}}}{2HBr} + \underset{\text{Sulphur.}}{S.}$$

As fast as the bromine which is in solution is taken up more is dissolved, until enough hydrogen bromide is formed to act as a solvent of the bromine, and thus enable the process to continue rapidly. This method cannot be employed for any but dilute solutions. The excess of hydrogen sulphide is removed by

* American Journal of Pharmacy, 1878, p. 116.

evaporation, and the sulphur which separates is removed by filtration.

Fothergill's process is intended to furnish extemporaneously a solution of about 10 per cent. strength. It consists in taking 10 grammes of potassium bromide and 12 grammes of tartaric acid, each in 30 c.c. of distilled water, mixing, cooling, and, after standing one hour, pouring on a muslin strainer and washing with a little ice-cold water.

The impurities in diluted hydrobromic acid are usually accidental, and due to carelessness in manufacturing. Sulphuric acid, which might be present from this cause, is easily detected by solution of barium chloride. Hydrochloric acid is found by the partial or complete solubility, in ammonium hydrate, of the precipitate with silver nitrate. On evaporating the acid there should be no residue. This last test would detect the potassium bromide and bitartrate, which are found in the acid when made by Fothergill's formula.

Bromides.—The salts of hydrobromic acid and bromine are called bromides. Many of them can be prepared by the action of the acid on a carbonate, hydrate, or oxide ; but they are oftener made from bromine, by first combining it with a metal like iron, and then decomposing by a carbonate or hydrate.

Potassium, sodium, lithium, and ammonium bromides are used medicinally, and silver bromide is used extensively in photography. Nearly all the bromides are soluble in water, the notable exceptions being those of silver, mercury, and lead. Heat fuses and volatilizes the bromides, most of them with decomposition, accompanied by liberation of bromine. They are all decomposed by chlorine, sulphuric and nitric acids.

Both the acid and its salts are detected by the addition of a dilute solution of starch and chlorine water, which form the yellow starch bromide. The bromine is easily soluble in, and separated by agitation with, ether, chloroform, and carbon disulphide ; to all of these it imparts a reddish-brown color, the shade of color depending on the concentration.

BROMINE AND CHLORINE.

Bromine Monochloride.—When chlorine is passed into bromine at a low temperature, large quantities are absorbed, and a reddish-yellow volatile liquid, bromine monochloride, BrCl, is formed. It is soluble in water, and separates a hydrate on cooling to 0°. It is decomposed at or above 10°.

IODINE.

Symbol, I. *Atomic Weight*, 125.89. *Valence*, I.

History.—In 1811, Courtois, a soap-boiler of Paris, noticed a peculiar corrosion of his copper kettle during the evaporation of kelp liquor, after crystallizing the sodium carbonate from it; and subsequently he obtained violet vapors on the addition of sulphuric acid to some of the waste liquor.

This discovery was announced in 1812. Davy and Gay-Lussac both investigated the new element about a year later, and the latter gave it the name of iodine from the violet color of its vapor.

Occurrence.—Iodine does not occur in the free state in nature, but in combination with potassium, sodium, or magnesium; it is found in the waters of many mineral springs, in sea water, in most sea plants and animals, in rock-salt, and in coal. In certain minerals it occurs combined with silver, lead, mercury, and zinc. The sodium nitrate, or Chili saltpetre, of Peru and Chili, contains iodine in the form of sodium iodate.

Source.—The world's supply of iodine comes from two sources, sea plants and Chili saltpetre. The former of these has been worked since the first demand for the element. The relative quantity occurring in sea water is too minute for that to be considered a source, but certain sea plants absorb the iodides in considerable quantity. Of these the *Algæ* have the greatest absorbing power, and two or three species of *Laminaria* are said to furnish the only weeds now used in this industry.

Preparation.—The sea-weeds which collect on the coasts of Scotland, Ireland, and some of the neighboring islands are gathered, and, with those brought in vessels sent out for the purpose, are burned, the ash forming what has for a long time been known as *kelp*. The similar product from the coasts of Normandy and the Channel Islands is called *varec*, and that from the Spanish coasts is known as *barilla*. These three commercial products were long worked for their sodium carbonate, but at the present time they are worked for the iodine they contain. The method of manufacture may be briefly outlined as follows:

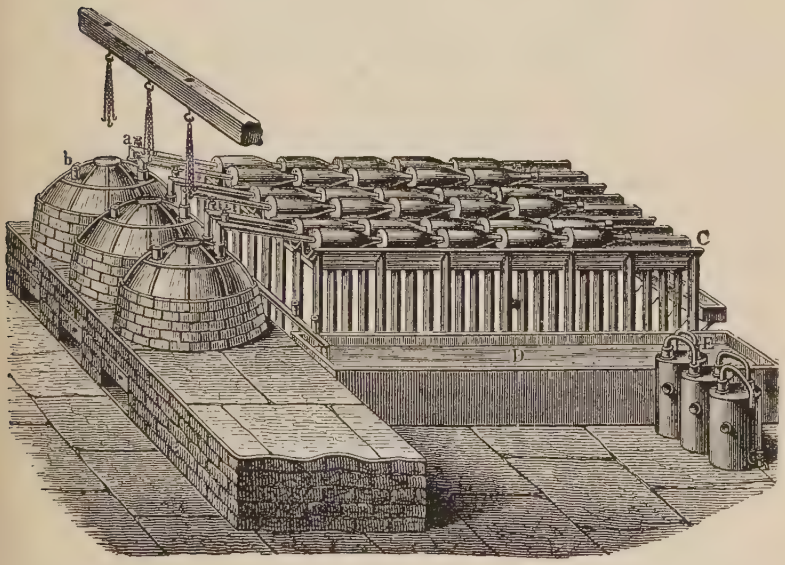
Sea-weeds are burned to a fused mass of carbon and ash; this mass is lixiviated with water, the solution evaporated to remove chlorides, sulphates, and carbonates, and the concentrated mother liquor treated with sulphuric acid, which causes a separation of sulphur on account of the sulphides and sulphites present. This sulphur and the crystals of sulphate formed are removed, and the

remaining acid liquor, in a lead-lined retort, is treated with manganese dioxide, which, with the free sulphuric acid previously added, liberates iodine according to the following reaction :

$$\underset{\text{Potassium Iodide.}}{2KI} + \underset{\text{Manganese Dioxide.}}{MnO_2} + \underset{\text{Sulphuric Acid.}}{2H_2SO_4} = \underset{\text{Potassium Sulphate.}}{K_2SO_4} + \underset{\text{Manganous Sulphate.}}{MnSO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Iodine.}}{I_2}.$$

The temperature is kept at about 60°, which causes the iodine to pass off in vapor and condense in a series of earthenware receivers adapted to the retort for that purpose. The apparatus by which the sublimation and condensation are accomplished is shown in Fig. 102. After iodine ceases to be evolved, bromine is

FIG. 102.



Sublimation of iodine.

liberated and conducted into separate receivers. The above method has been carried out at Glasgow, which has always been the seat of the iodine industry. Within the last few years, however, competition with the cheaper sources in Peru and Chili has led to improvements in the manner of heating the sea-weed, so as to reduce the loss by decomposition and volatilization, and at the same time the by-products are saved and utilized. In one of these, the "char" process, the sea-weed is heated in iron retorts at a low temperature. Acetic acid, tar, and ammonia distil over,

all of which can be utilized, while in the retort there remains a large quantity of charcoal, which, after treatment with water to remove iodides and other salts, can be used. Another, the "wet" process, consists of a still more radical change. The air-dried sea-weed is boiled with a solution of sodium carbonate and filtered; the precipitate or insoluble portion remaining on the filter is composed largely of cellulose. The filtrate is acidified with sulphuric acid, by which algin is precipitated. The solution, after removal of algin, is neutralized with calcium carbonate, evaporated, the easily crystallized salts removed, and the mother liquor treated for iodine in the usual manner. This process, in addition to increasing the yield of iodine, reduces the cost materially by the value of the algin and cellulose, both of which are useful in many ways.

In France chlorine is employed to separate the iodine from the liquor, instead of sulphuric acid and manganese dioxide, as follows:

$$\underset{\text{Potassium Iodide.}}{2KI} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Potassium Chloride.}}{2KCl} + \underset{\text{Iodine.}}{I_2}.$$

The most important sources of iodine at the present time are the nitre beds of Chili and Peru. So great has become this industry in South America that the yearly output from that source amounts to over a million pounds. The iodine exists in the mother liquor from the sodium nitrate in the form of sodium iodate, $NaIO_3$; from which it is precipitated by sodium bisulphite and sulphurous oxide, as follows:

$$\underset{\text{Sodium Iodate.}}{2NaIO_3} + \underset{\text{Sodium Bisulphite.}}{4NaHSO_3} + \underset{\text{Sulphur Dioxide.}}{SO_2} = \underset{\text{Sodium Bisulphate.}}{4NaHSO_4} + \underset{\text{Sodium Sulphate.}}{Na_2SO_4} + \underset{\text{Iodine.}}{I_2}.$$

The iodine is collected on muslin strainers, dried, and purified by sublimation.

According to another method, the sodium iodate is first reduced to iodide, as follows:

$$\underset{\text{Sodium Iodate.}}{NaIO_3} + \underset{\text{Sodium Bisulphite.}}{3NaHSO_3} = \underset{\text{Sodium Bisulphate.}}{3NaHSO_4} + \underset{\text{Sodium Iodide.}}{NaI}.$$

This sodium iodide is then treated with copper sulphate and ferrous sulphate, which precipitate the iodine as cuprous iodide:

$$\underset{\text{Sodium Iodide.}}{2NaI} + \underset{\text{Copper Sulphate.}}{2CuSO_4} + \underset{\text{Ferrous Sulphate.}}{2FeSO_4} = \underset{\text{Cuprous Iodide.}}{Cu_2I_2} + \underset{\text{Sodium Sulphate.}}{Na_2SO_4} + \underset{\text{Ferric Sulphate.}}{Fe_2(SO_4)_3}.$$

The cuprous iodide is collected and heated with manganese dioxide and sulphuric acid, and the iodine sublimed therefrom in the usual manner.

Iodine for medicinal purposes is purified by washing with cold water, drying, mixing with some potassium iodide, and subliming.

Properties.—Iodine, U.S.P., consists of "heavy, bluish-black, dry and friable rhombic plates, of a metallic lustre, a distinctive odor, a sharp and acrid taste, and a neutral reaction." It has a specific gravity of 4.948 at 17°, melts at 114°, and boils at about 184°, giving off a vapor which, when mixed with air, is violet-colored, but when pure is deep blue. At ordinary temperatures slow volatilization takes place without previous melting being recognizable, and, if in a bottle, minute crystals are deposited on the sides. Below 600° the vapor has a density of 126.86 (H = 1), which indicates that the molecule consists of two atoms, I_2, but above 600° the vapor density diminishes until 1500° is reached, when it has fallen to 65.7, or a little above the theory for I_1, which indicates that dissociation occurs at high temperatures.

Iodine is slightly soluble in water, one part of the element requiring 5524 parts of water at 10° to dissolve it, forming a peculiar yellowish solution, which, on exposure to light, forms hydriodic acid. The solubility of iodine in water is much increased by the presence of potassium iodide or hydriodic acid. The official **Liquor Iodi Compositus,** U.S.P. (Lugol's Solution), is a preparation based on this property. In strong alcohol iodine is soluble to the extent of one part to ten of the solvent, forming a dark-brown liquid, which is stronger than the **Tinctura Iodi,** U. S. P., which contains seven parts of iodine in one hundred of alcohol. Iodine is also soluble in ether, chloroform, carbon disulphide, benzene, and petroleum, to all of which, in small quantity, it imparts a red or violet color, according to the amount dissolved. It is also soluble in glycerin and in glacial acetic acid. The solubility is increased in water by a number of organic substances, notably tannic acid.

In chemical properties iodine resembles chlorine and bromine, although it is much less energetic. It bleaches, although slowly, and combines directly with hydrogen, chlorine, sulphur, phosphorus, and many of the metals. When a crystal of iodine is laid on a small piece of phosphorus the combination is attended with so much heat as to inflame the latter. As in the case of

bromine, sodium and iodine can be heated together without change, while with potassium the action is explosively rapid.

With starch solution a trace of iodine forms a deep blue color. This color is destroyed on heating and reappears on cooling. The compounds of iodine do not produce this color with starch until a little chlorine is added to liberate the iodine ; an excess of chlorine destroys the color because of the formation of iodine chloride.

Uses.—Iodine is used extensively in the manufacture of some of the coal-tar colors, in the preparation of iodides, in photography, and in medicine.

Impurities and Tests.—Fixed impurities, as coal, plumbago, etc., may be recognized by volatilizing a small quantity of the sample, which should leave no residue. An excess of moisture is indicated by the iodine adhering to the sides of the bottle, and by it failing to form a perfectly clear, limpid solution with chloroform. *Iodine chloride* is detected on agitating a sample with water, to which not more than a yellowish-brown color should be imparted. Compounds of iodine with chlorine, bromine, and cyanogen may be detected by triturating one part of iodine with twenty parts of water and filtering the solution. To one-half of the solution carefully add decinormal sodium hyposulphite solution until the solution is just decolorized. Then add a few drops of ferrous sulphate solution, and subsequently a little sodium hydrate, and heat the mixture gently. On now adding a slight excess of hydrochloric acid, the liquid should not assume a blue color, indicating the absence of *iodine cyanide*. To the other half of the aqueous filtrate add a slight excess of silver nitrate solution, shake actively and allow the precipitate to subside, and, having poured off the clear supernatant liquid completely, shake the precipitate with a mixture of 1 c.c. of ammonia water and 9 c.c. of water, and filter. Upon the addition of a slight excess of nitric acid to the filtrate not more than a slight opalescence should make its appearance, indicating the limit of *chlorine* or *bromine*.

PRACTICAL EXERCISES.

(1) Pass chlorine into a dilute (about one per cent.) solution of potassium iodide ; the liquid will become dark in color, owing to separation of iodine. In stronger solutions the iodine would be precipitated.

(2) To a portion of the iodine solution, diluted with water, add solution of starch ; a blue color will form, due to the combination of starch with iodine. When a precipitate is formed instead of a blue color, it is an

indication that the iodine solution is too strong, and a more dilute one must be used. The blue color of the starch iodide is destroyed by heat and by excess of chlorine.

(3) To another portion of the iodine solution in a test-tube add a small quantity of chloroform and agitate ; the chloroform will remove the iodine from the water, and settle to the bottom of the tube as a deep violet-colored liquid, and the water above will become nearly colorless.

IODINE AND HYDROGEN.

HYDROGEN IODIDE. HYDRIODIC ACID.

Formula, HI. *Molecular Weight*, 126.89.

Preparation.—A mixture of equal volumes of hydrogen and iodine vapor, passed over platinized asbestos heated to redness, partly combines, forming hydrogen iodide. This reaction does not take place nearly so readily as in the case of hydrogen and chlorine, or even hydrogen and bromine ; and the combination only imperfectly takes place when hydrogen is burned in iodine vapor.

As with hydrogen bromide, the method with amorphous phosphorus is the best for obtaining the gas in quantity. One part of amorphous phosphorus is mixed with fifteen parts of water in a suitable flask, and twenty parts of iodine are gradually added, keeping the flask cool, with ice if necessary, and allowing the action after each addition to cease before adding more. When all the iodine has been added, and action has finally ceased, gentle heat may be applied, and the gas, which is very heavy, collected by downward displacement. The same precautions of passing the gas over a mixture of amorphous phosphorus and broken glass may be observed here as with hydrogen bromide. Mercury is acted on by hydriodic acid gas, and, therefore, cannot be used for the collection. The reaction is as follows :

$$\underset{\text{Phosphorus.}}{P_4} + \underset{\text{Iodine.}}{6I_2} = \underset{\substack{\text{Phosphorus}\\\text{Tri-iodide.}}}{4PI_3}.$$

$$\underset{\substack{\text{Phosphorus}\\\text{Tri-iodide.}}}{4PI_3} + \underset{\text{Water.}}{12H_2O} = \underset{\substack{\text{Hydriodic}\\\text{Acid.}}}{12HI} + \underset{\substack{\text{Phosphorous}\\\text{Acid.}}}{4H_3PO_3}.$$

Another method, used when a solution of the gas in water is desired, consists in passing hydrogen sulphide into water containing powdered iodine :

$$\underset{\text{Iodine.}}{2I_2} + \underset{\substack{\text{Hydrogen}\\\text{Sulphide.}}}{2H_2S} = \underset{\substack{\text{Hydrogen}\\\text{Iodide.}}}{4HI} + \underset{\text{Sulphur.}}{S_2}.$$

The small quantity of iodine in solution is first converted into hydrogen iodide, which in turn dissolves more iodine to be acted on. Sulphur is deposited at the same time, and to prevent it enclosing the iodine, it is preferable to agitate, and add the latter in small portions at a time. The solution must be boiled to separate the excess of hydrogen sulphide, and filtered to remove sulphur.

Hydrogen iodide may also be prepared by heating together phosphoric acid and potassium iodide:

$$\underset{\text{Potassium Iodide.}}{3KI} + \underset{\text{Phosphoric Acid.}}{H_3PO_4} = \underset{\text{Potassium Phosphate.}}{K_3PO_4} + \underset{\text{Hydrogen Iodide.}}{3HI.}$$

The use of sulphuric instead of phosphoric acid in this process is precluded on account of the reduction of the sulphuric acid, according to the following reaction:

$$\underset{\text{Potassium Iodide.}}{2KI} + \underset{\text{Sulphuric Acid.}}{3H_2SO_4} = \underset{\substack{\text{Acid Potassium} \\ \text{Sulphate.}}}{2KHSO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\substack{\text{Sulphur} \\ \text{Dioxide.}}}{SO_2} + \underset{\text{Iodine.}}{I_2.}$$

Properties.—Hydrogen iodide is a colorless, heavy gas, with a sharp, irritating odor, and an acid taste and reaction. At 0° and a pressure of four atmospheres it forms a colorless liquid, which solidifies at —51°. Its specific gravity is 4.42. The gas is very soluble in water, and when saturated at 0° the solution has a specific gravity of 1.99.

Both the strong and weak solutions vary in boiling point until the strength of 57.75 per cent. is reached, when it distils at 127°, under ordinary atmospheric pressure. The gas commences to decompose at 180°, and if some of it be poured down on the flame of a Bunsen burner, clouds of iodine vapor are evolved. It also readily decomposes when a red-hot platinum wire is plunged into a vessel of it, or more slowly when simply exposed to the air. This accounts for the difficulty of preparing the gas by the direct union of the elements. The aqueous acid readily decomposes on exposure to light, and becomes dark brown in color; for this reason a syrup of it has been made official, instead of the acid of 1860, in order to take advantage of the preservative action of sugar.

Uses.—The acid has some use in medicine, and is also much employed in chemical operations where a reducing agent is desired, on account of the readiness with which it is decomposed, giving hydrogen in the nascent state.

Iodides.—These salts, like the bromides, may be prepared from the acid, but it is cheaper to make them directly from the element. They are nearly all soluble in water, the important exceptions being the silver, mercurous, mercuric, and lead iodides. Heat fuses and decomposes the iodides, with formation of the metal or its oxide and free iodine.

Detection.—The acid and its salts are detected by the addition of starch and chlorine water, when, if the starch solution be sufficiently dilute and the chlorine in not too great excess, there will be formed the blue starch iodide. This blue color disappears on heating and reappears on cooling, and is destroyed by an excess of chlorine water. When the blue mixture is agitated with ether, chloroform, or carbon disulphide, the iodine is withdrawn, imparting to the solvent a red or violet color, according to the amount present. Before deciding finally on the presence of hydriodic acid and iodides, one must be sure that such salts as the sulphites and thiosulphates are either absent or are completely oxidized by the chlorine, for the blue color will not appear until all readily oxidizable substances are converted. A few organic substances, notably tannin, interfere with the formation of the blue color. When bromides are present with iodides, the color resulting from the addition of starch and chlorine water will be green, from a mixture of the yellow starch bromide with the blue starch iodide.

IODINE AND CHLORINE.

These two elements unite in two proportions, forming iodine monochloride, ICl, and iodine trichloride, ICl_3. The former is prepared by passing dry chlorine over dry iodine, until the latter is liquefied, or by distilling one part iodine with four parts potassium chlorate, or by boiling iodine with strong aqua regia, diluting with water, and agitating with ether. The ether dissolves the iodine chloride, and leaves it behind on evaporation. It is a thick, reddish-brown liquid, which solidifies, on standing, to well-defined crystals, which melt at 24.7°. It is decomposed by water, forming iodic acid, hydrochloric acid, and free iodine. As might be expected, it does not color solution of starch, on account of the presence of chlorine.

Iodine trichloride is prepared by continuing the passing of chlorine over the iodine monochloride until a solid compound is obtained. This is a solid, crystalline compound, of a yellow color, which, when heated to 25°, gives off chlorine, forming the monochloride. It partly dissolves in water, and is in part decomposed into iodic and hydrochloric acids and free iodine. A solution is prepared for medicinal use by suspending 5.5 grammes of iodine in 22 grammes of water, and passing in chlorine as long as it is absorbed by the well-cooled mixture.

The solution contains 10 grammes of iodine trichloride.

For testing, the aqueous solution (1 to 20) is agitated with chloroform, which must not be colored violet at once, but the color should appear immediately on the addition of a few drops of stannous chloride.

FLUORINE.

Symbol, F. *Atomic Weight*, 18.9. *Valence*, I.

History.—In the latter part of the eighteenth century, Marggraf noticed that his retort was powerfully attacked when he heated in it a mixture of fluor-spar and sulphuric acid. Ampère, in 1810, pointed out the analogy between hydrochloric acid and the compound at that time called fluoric acid; hence, when adapted to more modern nomenclature, the name of this peculiar compound became hydrofluoric acid.

Many attempts have been made in recent years to isolate the element. Its action on the vessels containing it and its intense affinity for moisture prevented its separation in the free state in such a quantity and degree of purity as to be of any value.

In 1886, Moissan, by passing a powerful electric current through anhydrous hydrofluoric acid, liquefied at 0° and cooled to −23°, and contained in a U-shaped tube of platinum, succeeded in obtaining the free element as a colorless gas. A small quantity of potassium fluoride was added to the acid to make it a better conductor, and the positive pole, at which the element appeared, was an alloy of platinum and iridium. The platinum tube in which the operation was carried out was not acted on perceptibly at such a low temperature. In 1897 Moissan and Dewar, using liquid oxygen as a refrigerant, succeeded in liquefying fluorine. The temperature at which this takes place is given by them as −180°.

Occurrence.—Fluorine is said to occur in the free state in the crevices of certain fluor-spar deposits in Bavaria. It is, however, in minute quantity only and recognized by its odor. It occurs combined in a number of minerals, chiefly as calcium fluoride or fluor-spar, CaF_2, and as sodium and aluminum fluoride or cryolite, $6NaF.Al_2F_6$. The former of these is pretty well distributed over the globe, the latter is found in Greenland. Fluorine has been found in small quantity in sea water, in many mineral waters, in the bones and teeth of man, and in milk.

Preparation and Properties.—The preparation has been sufficiently described under its history. Fluorine is a colorless gas, with an odor resembling hypochlorous acid. It is the most

powerful of all the known elements ; gold, platinum, with, perhaps, a few other of the noble metals, and oxygen are not attacked by it. It combines explosively with hydrogen in the cold, and decomposes the alkali chlorides, when they are anhydrous, liberating chlorine. Water is decomposed by it, with formation of hydrogen fluoride and ozone. Cork chars and ignites in the gas, and many organic substances, like benzene, alcohol, and turpentine, are inflamed on coming in contact with it. Its rapid action on many metals at ordinary temperatures is prevented by the formation of a coating of fluoride ; iron, however, completely absorbs it. Hydrogen, sulphur, phosphorus, iodine, arsenic, antimony, silicon, boron, potassium, and sodium combine with it on contact with great energy, attended by heat and light. When liquefied it forms a clear yellow liquid, possessed of great mobility. At the temperature of its liquefaction (—185°) it no longer attacks glass, nor does it displace iodine from iodides, although it still inflames benzine and oil of turpentine.

FLUORINE AND HYDROGEN.

HYDROGEN FLUORIDE. HYDROFLUORIC ACID.

Formula, HF. *Molecular Weight*, 19.9.

Preparation.—The pure anhydrous acid is prepared with considerable difficulty by heating the acid potassium fluoride in a platinum retort, connected with a condenser and receiver of the same metal. The principal difficulties arise from moisture, and from danger of inhaling the vapor, which is extremely irritating and poisonous. Sulphur has been used as a lute in making tight joints.

The diluted acid is more easily prepared from fluor-spar and sulphuric acid, in a leaden or platinum vessel. The vapor is conducted through a tube of the same metal into water in a lead. platinum, or gutta-percha vessel :

$$\underset{\text{Calcium Fluoride.}}{CaF_2} + \underset{\text{Sulphuric Acid.}}{H_2SO_4} = \underset{\text{Calcium Sulphate.}}{CaSO_4} + \underset{\text{Hydrogen Fluoride.}}{2HF.}$$

The pure anhydrous acid is a colorless liquid, having a specific gravity of 0.9879 at 15°. It boils at 19.4°, and at —102.5° solidifies to a crystalline mass which melts at —92.3°. Hydrogen fluoride does not act on glass as long as it is absolutely free from moisture, and the non-metals are but slightly affected by it. It

is very soluble in water, and the solution is understood in speaking of hydrofluoric acid. The most concentrated solution has a specific gravity of 1.25, and this on heating gives off the gas until the specific gravity is reduced to 1.15, when it distils unchanged at 120°, and contains 36 to 38 per cent. of the anhydrous acid. The aqueous acid rapidly attacks glass, combining with the silica as follows:

$$\underset{\text{Hydrogen Fluoride.}}{4HF} + \underset{\text{Silicic Oxide.}}{SiO_2} = \underset{\text{Silicon Fluoride.}}{SiF_4} + \underset{\text{Water.}}{2H_2O}.$$

On account of this property, one of the most important uses of the acid is in etching glass. That portion of the glass to be preserved from its action is covered with a film of wax or paraffin dissolved in turpentine oil. The divisions on thermometers, eudiometers, and other graduated apparatus are marked with its aid. The dilute commercial acid is transported in wooden vessels, and the more concentrated article in gutta-percha or paraffin (ceresin) bottles.

At a temperature of 30°, the density of hydrogen fluoride is such as to lead to the conclusion that, at that point and below, it exists as the double molecule, H_2F_2. Above that temperature it possesses the formula HF. This view is supported by the fact that some of its salts are acid in character; that is, only half of the hydrogen of the acid is replaced by a base, for instance, the one with potassium, used in its preparation, has the formula KHF_2.

THE HALOGEN GROUP.

The halogens constitute a distinctive group or family of elements, and present striking analogies in their physical and chemical properties. Also the same may be said of their various compounds with the other elements. Owing to the readiness with which they tend to form salts, analogous in physical properties to sea-salt, the name (ἅλς, ἁλός = *sea-salt*, γεννάω = *to produce*) *halogens* has been applied to the entire group.

Physical Properties.—

	F.	Cl.	Br.	I.
Atomic weight	18.9	35.18	79.34	125.89
Melting point		—102° C.	—7° C.	+113° C.
Boiling point		—33° C.	+63° C.	+200° C.
Density (liquid or solid) . .		1.33	3.18	4.97

The values of the physical constants of this group rise in ratio to the increase of atomic weight.

The density and boiling points of their hydrides exhibit a like gradation.

	HF.	HCl.	HBr.	HI.
Molecular weight . . .	19.9	36.18	80.34	126.89
Density	10	18.2	40.4	63.9
Boiling point		—83.7° C.	—64.9° C.	—34.1° C.

Chemical Properties.—The chemical deportment of these elements admits like comparisons. Thus, the comparative affinities of the halogens for hydrogen decrease in accordance with their increase in molecular weight. For example, fluorine and hydrogen combine in the dark, chlorine and hydrogen on exposure to sunlight, while bromine requires a temperature of 200° with sunlight, and iodine combines through the agency of platinum sponge. This same rule applies to the relative affinities of these halogens for the electro-positive elements and the comparative stability of their compounds. Taking them in the order of increasing atomic weight, each element is capable of displacing any one of those following, from its inorganic combination. Thus, fluorine displaces chlorine, bromine, and iodine. The facility with which this takes place increases with the atomic weight of the element. The stability and activity of the halogen acids present the same comparisons. Thus, hydrogen fluoride is the most stable and energetic in its chemic deportment, while hydrogen chloride requires a temperature much above 1500° C. for its decomposition; hydrogen bromide is less stable, and breaks up into its elements at 800° C.; the least stable hydrogen iodide decomposes at gentle heat. The comparative intensities of their chemical affinities and the stability of their salts decrease in like ratio.

From the preceding we have seen that the affinity of the halogens for hydrogen diminishes with increasing atomic weight from F to I. With their affinities for oxygen this is reversed. Where fluorine fails to combine with oxygen, the chlorine and bromine compounds are quite unstable; the iodine compounds are the most stable. This accounts for the fact that iodine will liberate chlorine and bromine from their higher oxygen compounds, the reverse of their deportment in the case of the hydrogen and metallic compounds of the halogens. We also find that the stability of the oxygen acids increases with the addition of oxygen. Thus, HClO, $HClO_2$, and HBrO are very weak and unstable, while the acids $HClO_4$, $HBrO_3$, and HIO_3 are energetic and very stable.

CHAPTER IV.

THE OXYGEN GROUP.

OXYGEN.

Symbol, O. *Atomic Weight*, 15.88. *Valence*, II.

History.—Oxygen was discovered by Priestley, of England, August 1, 1774, and a short time after, independently, by Scheele, of Sweden. Lavoisier gave it the name *oxygenium*—acid-former—under the impression that to it were due the acid properties of many bodies.

Occurrence.—Although oxygen does not occur alone and uncombined, it does exist in the atmosphere in the free state, mixed with four volumes of nitrogen.

In combination it occurs still more abundantly, eight-ninths of the water in the globe being composed of it, and it exists in large percentage in nearly all mineral substances. The statement has been made that one-half of the solid part of the earth is composed of this element. In combination with carbon and hydrogen, it forms the basis of nearly all the organic compounds in the vegetable kingdom.

Preparation.—(1) The original method of preparing oxygen, by heating mercuric oxide, as discovered by Priestley, is still useful for illustration:

$$2HgO = 2Hg + O_2.$$

(2) By heating a nitrate, as potassium nitrate:

$$2KNO_3 = 2KNO_2 + O_2.$$

(3) By the electrolysis of water:

$$2H_2O = 2H_2 + O_2.$$

(4) By heating manganese dioxide and sulphuric acid:

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2.$$

(5) When potassium dichromate and sulphuric acid are mixed, chromium trioxide is formed, according to the following reaction:

$$K_2Cr_2O_7 + 2H_2SO_4 = 2KHSO_4 + H_2O + 2CrO_3.$$

On heating this mixture with an excess of sulphuric acid, oxygen is liberated :

$$2CrO_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3H_2O + O_3.$$

(6) On heating an aqueous solution of bleaching powder—calcium hypochlorite—and cobaltous chloride to 70° or 80°, cobaltous oxide is formed, which in reacting on the calcium hypochlorite is converted into cobaltic oxide, and this in turn gives up oxygen :

$$Ca(ClO)_2 + 4CoO = CaCl_2 + 2Co_2O_3.$$
$$2Co_2O_3 = 4CoO + O_2.$$

(7) The method most used on a small scale at the present time consists in heating a mixture of four parts potassium chlorate and one part manganese dioxide. The action of the latter is either mechanical or catalytic, as the chlorate will yield oxygen when heated alone, provided the temperature is raised to 325°, and then slowly higher. The object of the mixture, however, is to obtain the gas at the lower temperature of 200°, and without fusion of the chlorate :

$$2KClO_3 = 2KCl + 3O_2.$$

This method is usually carried out in a copper or iron retort, with arrangements for feeding in about one pound of the mixture at a time, without disconnecting.

Every new lot of manganese dioxide should be tested, by heating a small quantity in a test-tube with some chlorate, in order to prove the absence of impurities of an organic character, which, if present, would cause an explosion when heated.

Manganese dioxide (MnO_2), which promotes the decomposition of the chlorate, undergoes little or no alteration during the process, while it is capable of yielding oxygen on heating ; yet the temperature of its decomposition is much higher than that of the chlorate. Cupric and ferric oxides likewise share this property of manganese dioxide. We have other instances in which a body promotes decomposition of substances without suffering any permanent change itself. For example, finely divided gold, platinum, carbon, and manganese dioxide decompose solutions of hydrogen peroxide into water and oxygen. Such phenomena are termed *catalysis*, and the substances which promote these reactions are *catalytic agents*.

(8) A number of processes have been proposed for preparing oxygen on a larger scale and at a lower cost than is possible

by the preceding. One of these, suggested by Deville and Debray, consists in allowing sulphuric acid to trickle into a retort filled with bricks and heated to redness. The decomposition takes place as follows :

$$2H_2SO_4 = 2SO_2 + 2H_2O + O_2.$$

The sulphur dioxide is removed by passing the mixture of gases through water, or up through a tower filled with coke, over which a small stream of water trickles. The sulphur dioxide may be utilized by converting it into sulphuric acid to be used again.

(9) The Tessie du Motay process heats manganese dioxide and sodium hydrate to 450° C. in a current of air, and then decomposes the sodium manganate so formed by heating in a current of steam, the original materials being left for renewed heating in air.

(10) Brin's process also consists in extracting the oxygen from the atmosphere. It was patented in 1880, and again in 1885, but still required the improvements of three or four years to bring it to a successful condition on a large scale. The principle involved is not new, having been proposed by Boussingault. It has long been known that many peroxides, notably that of barium, give up their oxygen at high temperatures, and regain it from the atmosphere on cooling.

The Brin process, as now perfected, consists in heating a porous barium oxide to 700° in closed vertical retorts, into which purified air is forced under a pressure of ten or fifteen pounds in excess of that of the atmosphere. The barium rapidly undergoes peroxidation, and, as soon as complete, the air-pressure is reduced to fourteen pounds below the atmospheric pressure, when oxygen is rapidly given off. The whole time occupied in the oxidation of the barium and in the recovery of the gas is said not to exceed ten minutes. One of the important conditions of this process is to have the barium oxide in a porous condition. This is attained by heating barium nitrate to 880° for three or four hours. Another condition is the use of pure air,—that is, free from carbon dioxide. This is accomplished by a system of washers containing lime and sodium hydrate. The oxygen obtained has a purity of from 90 to 96 per cent., and is conveyed into a large gas-holder, from which it is pumped into steel cylinders under a pressure of 800 to 1000 pounds, in which form it goes into commerce. The small cylinders contain forty gallons of the gas compressed to about the volume of one-half gallon.

Properties.—Oxygen is a colorless, odorless, and tasteless gas. It is slightly soluble in water, 100 volumes of the liquid at 0° dissolving 4.1 volumes of the gas. The specific gravity of oxygen is 1.10535 (air = 1), and its density 15.88 (H = 1). Under a pressure of 22.5 atmospheres and at a temperature of —136°, it liquefies, and in that condition has a specific gravity of 0.899 (water = 1). This liquid is colorless and boils at —184° under a pressure of 1 atmosphere. The critical temperature of oxygen is —118° C. and critical pressure 50 atmospheres. It is also distinctly magnetic.

In chemical properties oxygen is very active, combining either directly or indirectly with all the known elements except fluorine. It is not a combustible gas under ordinary circumstances, but it supports the combustion of many elements and compounds. The term combustibility is considered to refer to the power of a substance to continue burning in the air after being once ignited; that is, to combine with the oxygen of the atmosphere. When mixed with hydrogen the two explode violently on the application of flame or the electric spark, the result of the combination being water. With many other of the elements oxygen unites at ordinary temperatures, sodium, potassium, and phosphorus being examples; with others again, as sulphur, iron, carbon, and copper, an elevated temperature is required, while with platinum, gold, and silver, combination does not take place at any temperature. The products of these combinations are called *oxides*, those with the non-metals being *acid-forming oxides;* that is, capable of forming acids by combination with water (see p. 233), while most of those with metals are *basic oxides*, many of which form basic hydrates with water (*Ibid.*).

A great number of the compounds with which we will deal later are combinations of oxygen with some other element. As examples of the formation of oxides we may take the following:

Zn	+	O	=	ZnO,	Zinc oxide.
C	+	O_2	=	CO_2,	Carbon dioxide.
P_2	+	O_5	=	P_2O_5,	Phosphoric oxide.
Fe_3	+	O_4	=	Fe_3O_4,	Ferroso-ferric oxide.

All of these elements burn brilliantly in oxygen when once ignited; this is accomplished in the case of zinc and iron by attaching the glowing end of a match, and with phosphorus and carbon by bringing them in contact with flame a moment before introducing into the gas. In the act of respiration a chemical

process is involved, whereby certain organic constituents of the blood are consumed, with formation of carbon dioxide and water.

Uses.—The low cost at which oxygen can be produced by the Brin process has admitted of its application in a number of operations from which it has heretofore been excluded. Except in the nascent state, oxygen alone appears to have no bleaching action, but it has been found that a small proportion added to a solution of bleaching powder greatly increases the efficiency of the latter. In aging spirits, the gas has been found effective when forced into the liquid under a pressure of one or two atmospheres, and to accomplish in a short time what usually requires years by the ordinary method. It has also been found to assist in the removal of sulphur from illuminating gas when mixed with the latter previous to its passage over the lime. Oxygen gas when properly associated with hydrogen, or illuminating gas, is used in certain metallurgical operations where a high temperature is required, and for furnishing a brilliant light, as in the oxyhydrogen lantern. Although frequently tried, the use of oxygen in medicine has not been attended with very encouraging results.

AT PRESENT IT HAS ... FEB. 1904.

PRACTICAL EXERCISES.

(1) Prepare oxygen by placing a few crystals of potassium chlorate in a clean dry test-tube, adapt a delivery-tube long enough to reach under the surface in a vessel near by. Apply a steady flame, taking care not to allow any water to be drawn back into the tube; this may be accomplished by taking the end of the delivery-tube from the water before the flame is withdrawn. As soon as bubbles of gas escape freely, and the air has been expelled, bring a test-tube filled with water over the escaping gas and collect it.

The evolution of oxygen is effected more easily by mixing with the potassium chlorate, before heat is applied, about one-fourth its weight of manganese dioxide.

(2) Apply a lighted taper to a tube full of oxygen, the gas will not burn. Plunge the taper into the gas and it will burn with greatly increased energy. Extinguish the flame, leaving a glowing spark, and again plunge into the gas, the taper will be re-ignited. These experiments indicate the non-combustibility of oxygen under ordinary circumstances, but show that it is an active supporter of combustion.

(3) A piece of glowing charcoal is lowered into the gas; a rapid combustion ensues and the charcoal disappears. Pour some lime water into the tube, agitate well; a white precipitate of calcium carbonate is produced. If this be tried with oxygen, previous to the burning of the charcoal, no precipitate will be formed. A number of other substances, as phosphorus, sulphur, and iron, will, when once ignited, burn in oxygen with great brilliancy.

(4) Take two test-tubes, one about twice the capacity of the other. Fill the larger with hydrogen and the smaller with oxygen, bring their mouths together, and, after turning once or twice to thoroughly mix their contents, open their mouths to a flame. A sharp report is caused by the combination to form water. If more than two volumes of hydrogen to one of oxygen be present, the surplus remains uncombined; if oxygen be present in greater proportion, the excess of it remains.

OZONE.

Formula, O_3. *Molecular Weight*, 47.64.

History.—This peculiar substance was first noticed by Van Marum, in 1785, in passing electric sparks through oxygen, of which it appears to be only a modification. Schönbein, in 1840, gave it the name *Ozone*, from Greek ὄζω, signifying "I smell."

Occurrence.—Ozone is found in minute quantities in the atmosphere which is remote from large cities, and is especially noticeable after a thunder-storm. It is also supposed to be produced by the growth of plants.

Preparation.—(1) Ozone is evolved at the positive pole in the electrolysis of water acidified with sulphuric and chromic acids. (2) It is also formed by the silent discharge of electricity through air or oxygen. For this purpose a Siemens' ozonizing tube is employed. (3) When phosphorus is allowed to slowly oxidize in the air. This is best accomplished by standing two or three sticks of phosphorus on end in a dish containing a shallow layer of water, so that they are about one-half immersed in the liquid. A stoppered bell-jar is then placed over the whole, and very soon ozone may be detected by the appropriate tests.

It is difficult to obtain a definite volume of ozone, since it is always mixed with air or oxygen, but it may be accomplished by passing the mixture of ozone and oxygen from a Siemens' apparatus through a tube cooled with liquid oxygen to —181°, when the ozone separates as a steel-blue liquid, boiling at —106°.

Properties.—Ozone is a colorless gas with a peculiar, irritating odor. It possesses very active oxidizing powers, attacking most organic matter, and oxidizing many of the metals, like mercury and silver. It liberates iodine from potassium iodide, and this property is turned to account in the following test: Paper is saturated with solutions of potassium iodide and starch, and then dried. This paper becomes blue in the presence of a trace of

ozone ($2KI + H_2O + O_3 = 2KOH + I_2 + O_2$). Of course, chlorine and the higher oxides of nitrogen must be avoided.

At a temperature of 237° ozone is converted into ordinary oxygen; this change takes place, though slowly, at much lower temperatures.

Composition.—It has been shown in several ways that ozone is an allotropic form of oxygen, in which three atoms combine to form a molecule instead of two; consequently, in its formation three volumes of oxygen condense and form two volumes of ozone.

The preparations known as "ozonized water," "pyrozone," are mainly solutions of hydrogen peroxide (see p. 237).

Uses.—Various uses have been suggested for ozone, chiefly in the industrial process of bleaching. It has also been used as a disinfectant and somewhat as an oxidizing agent in industrial processes.

OXYGEN AND HYDROGEN.

These elements combine in two proportions:

Hydrogen monoxide, or Water, H_2O.
Hydrogen dioxide, H_2O_2.

WATER.

Formula, H_2O. *Molecular Weight*, 17.88.

History.—When Cavendish, in 1766, discovered hydrogen, it opened the way for breaking down the ancient belief in the elementary nature of water. This he followed up by exploding a mixture of hydrogen and air with the electric spark, and suggesting that hydrogen and oxygen, in the proportions of two volumes of the former and one of the latter, combine to form water. This was confirmed by Lavoisier, in 1783, who decomposed water into its elements and decided that it was composed of one part, by weight, of hydrogen, and eight parts, by weight, of oxygen. Gay-Lussac and Humboldt, in 1805, confirmed these experiments and those of Cavendish.

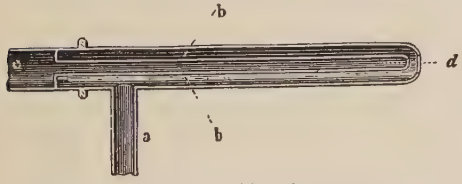
Occurrence.—In addition to the abundant natural occurrence, as we are accustomed to see it, water is very widely distributed in such a way as to escape casual observation. All plants and animals contain it in large amount, and considerable quantities exist in the atmosphere.

Formation.—The simplest method of forming this compound from its elements, hydrogen and oxygen, and proving the product

to be water, is to burn a jet of hydrogen in air, and hold over the flame a cool bell-jar, which will immediately become coated with a film of moisture. When a mixture of the two gases is brought in contact with flame, a violent explosion results. If, however, they are brought together at the moment of their combination, so as to prevent explosion, the mixture will burn with a very intense heat. The apparatus by which this is accomplished is illustrated in Fig. 103, and it is known as the oxyhydrogen blowpipe. The hydrogen is introduced through the tube *a* and ignited at *d*; oxygen is then introduced through *c*. When the jet is directed against a piece of freshly-burned lime, we have the oxyhydrogen lamp, the incandescent lime of which gives an intense light.

Synthesis.—The synthesis of water is accomplished by the use of Ure's eudiometer tube, Fig. 104. The tube, having been filled with water or mercury, is connected with an oxygen supply and a definite amount of this gas run into the closed limb; in the same manner twice as much hydrogen is introduced, the measurements being made with the columns of liquid in the two limbs at exactly the same height. A small air-space is left in the open end of the tube to act as a cushion. The aperture is then

FIG. 103.



Oxyhydrogen blowpipe.

FIG. 104.

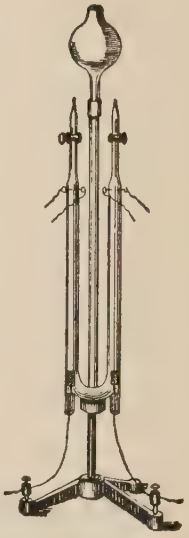
Ure's eudiometer.

tightly closed with the thumb, and an electric spark passed through the mixed gases, by means of the platinum wires, which are fused into the closed end. A slight flash appears on the passage of the spark, and immediately suction is felt by the thumb. On removing the latter carefully, and filling the open limb with the additional amount of water necessary, the gases in the closed limb will be found to have disappeared. It is, perhaps, more striking to explode equal volumes of the two gases, when it will be found that a quantity equal to one-half of the oxygen introduced remains, which may easily be proved to be that gas by applying a glowing taper.

Analysis.—For the purpose of determining the composition of water by analysis, the apparatus illustrated in Fig. 105 is best adapted. The tubes are filled with water, to which a little sulphuric acid has been added to make the liquid a better conductor of electricity. On attaching the wires from the opposite poles of a battery of two or more cells, a steady current of the two gases will rise in the two closed limbs of the apparatus. It will be found, on testing, that one of these gases, that from the negative electrode, will burn and otherwise respond to the tests for hydrogen, while the other, from the positive electrode, will ignite a glowing taper and show the other tests for oxygen. The hydrogen, it will also be noticed, occupies just twice the space filled by the oxygen.

Properties.—Pure water is an odorless and tasteless liquid. In small quantities it is colorless, but in larger volume it has a bluish color. On cooling the water to 0°, it solidifies, or, rather, crystallizes, in the hexagonal system; on the application of heat, it boils at 100° under the ordinary atmospheric pressure of 760 millimeters of mercury. Water, at a certain temperature, affords an exception to the rule that bodies expand with heat and contract on cooling. At 4° it reaches its greatest density, and below, to the solidifying point at 0°, it expands. On account of this peculiar property, ice floats on water instead of sinking, as it otherwise would.

FIG. 105.



Electrolytic decomposition of water.

The specific gravity of water at its greatest density, 4°, is 1.000, and at 0° it is 0.99987. The melting temperature of ice is quite constant, but under certain conditions, for instance, under pressure, the freezing may not take place until several degrees below zero have been reached. The boiling point of water bears a constant relation to the pressure. Under one atmosphere (the ordinary pressure) the boiling point is constant: the application of more heat only causes the liquid to boil faster, but does not increase its temperature. When, however, the liquid is confined under a pressure of two atmospheres, the temperature will rise on the application of heat to 120.6°, when boiling will commence.

The following table gives the temperature at which water boils under an increase of pressure:

Pressure in atmospheres.	Boiling point.	Pressure in atmospheres.	Boiling point.
1	100°	6	159°
2	120.6°	8	170.8°
3	133.9°	10	180.3°
4	144°	25	224.7°

Below the ordinary boiling point of water the pressure is best expressed in millimeters of mercury, as follows:

Pressure in millimeters of mercury.	Boiling point.	Pressure in millimeters of mercury.	Boiling point.
760.000	100°	17.391	20°
525.450	90°	12.699	15°
354.280	80°	9.165	10°
233.093	70°	6.534	5°
148.791	60°	4.600	0°
91.982	50°	2.093	—10°
54.906	40°	0.927	—20°
31.548	30°		

Water combines with many bodies with considerable energy. Of these the most striking are certain basic oxides, as potassium oxide, K_2O, and calcium oxide, CaO, which form hydrates as follows:

$$K_2O + H_2O = 2KOH,$$
$$CaO + H_2O = Ca(OH)_2.$$

With certain acid oxides it combines energetically to form acids, as follows:

$$SO_3 + H_2O = H_2SO_4,$$
$$P_2O_5 + 3H_2O = 2H_3PO_4.$$

In all these cases considerable heat is developed.

Water is a very stable compound, withstanding a temperature of 1000°; above this point, dissociation takes place. Some elements, like potassium, sodium, or calcium, decompose it at ordinary temperature with evolution of hydrogen:

$$K_2 + 2H_2O = 2KOH + H_2.$$

Heavy metals, such as zinc, iron, and nickel, decompose water, when passed as steam over the red-hot metal:

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

Water enters into the composition of many bodies as *water of crystallization*, some in a remarkable degree, as sodium phos-

phate, $Na_2HPO_4 12H_2O$, which at 100° loses all its water, amounting to 60.31 per cent., and alum, $K_2Al_2(SO_4)_4 24H_2O$, which at 200° loses all its water, amounting to 45.54 per cent.

Water comes nearer than any other liquid to being a universal solvent, for which purpose, on account of its stable nature, it is especially adapted.

The foregoing description refers to a pure water as prepared by distillation, but water may be further considered under the following different varieties:

Distilled water.

Rain water.

Spring and mineral waters.

Sea water.

(1) **Distilled Water.**—Ordinarily the distillation of this liquid is accomplished by boiling a good, natural water and passing the vapor into a block tin or glass condenser. The first portions which come over contain certain gases and should be rejected; then a quantity amounting to about 80 per cent. of the whole should be collected in glass-stoppered bottles and preserved for use. The residue in the still contains the solid impurities, and should be washed out before another portion of water is put in. When thus prepared, distilled water should possess the physical and chemical properties previously described, and should leave no residue when one liter is evaporated in a porcelain or platinum dish.

Tests.—The following tests, in addition to the evaporation of some of the liquid as above described, would prove the absence of all probable impurities. A few drops of lead acetate solution should produce only a faint turbidity, and when another portion is mixed with an equal volume of calcium hydrate solution no cloudiness should appear, showing the absence of carbonic acid. No turbidity should develop, after some hours' standing, with a small quantity of barium chloride solution,—absence of sulphuric acid. No opalescence should appear on addition of silver nitrate, —absence of chlorine. Nitric acid may be detected by mixing ten to twenty parts of the water with one or two parts of concentrated sulphuric acid and one drop of indigo solution; the blue color should not disappear on heating to 100°. From 10 to 20 c.c. of the water should give only a faint yellowish color with five drops of Nessler's reagent (potassio-mercuric iodide), indicating the absence of ammonia compounds. Organic matter may be detected by adding to 100 c.c. of the water 1 c.c.

of concentrated sulphuric acid, heating to 100°, and adding a few drops of a dilute solution (1–100) of potassium permanganate, when the red color imparted by the latter should not be destroyed after some hours' standing in a well-closed vessel.

(2) **Rain Water.**—This is the purest form of natural water, provided it can be collected without contamination. Under ordinary circumstances it becomes impure from the atmospheric gases, especially in the vicinity of large cities; of these, carbon dioxide is the most abundant, although sulphurous oxide is also present in considerable quantity. Rain water is usually collected from roofs, on which there is ordinarily more or less dust and other foreign matter; this renders the water impure, unless the first portions that fall can be run off and rejected. When properly collected, rain water is one of the most satisfactory for washing purposes, but is rather unpalatable for drinking.

(3) **Spring Water.**—The water-supply of cities is usually taken from lakes or rivers, while that in country districts is taken from wells or springs. The water from these sources, having been in contact with the earth, holds in solution small quantities of mineral compounds, frequently calcium sulphate or carbonate, with varying amounts of organic matter. The fitness of a water for domestic purposes is usually determined by the amount of organic matter present, and more exactly by an estimation of the nitrogen of this organic matter. The water from the large lakes is considered purest, while that from rivers is often quite impure on account of sewage contamination from sources higher up the stream. Water from wells in cities should never be used for domestic purposes unless it is taken from a bored well, cased in and of such depth as absolutely to insure its freedom from surface drainage.

After the freedom of a water from organic matter has been established, the question of *hardness* is still an important factor in determining its value for domestic purposes. When calcium and magnesium salts are present in a water they form insoluble precipitates with soap, which are inconvenient in washing; such a water is called *hard*, and requires the use of a great deal more soap in order to produce lather. These salts are usually sulphates or carbonates, frequently both, the latter being held in solution by the carbon dioxide present. When the hardness is due to sulphate, it is said to be *permanently hard*, in distinction from that which contains carbonates held in solution by carbon dioxide,

which is termed *temporarily hard*. In the latter case it becomes a soft water by simply boiling, which drives off the carbon dioxide and precipitates the salts as carbonates. Water is said to have one degree of hardness when it contains one part of calcium carbonate or its equivalent in one hundred thousand. The degree of hardness is determined by agitating the sample of water with a standard solution of soap until a permanent lather is produced. The standard solution of soap is prepared by agitation with calcium chloride solution of known strength. "Each degree of hardness indicates the destruction and waste of twelve parts of the best hard soap by one hundred thousand parts of water." (Frankland.)

Mineral Waters may be considered a class of spring waters, since they are found either in springs or wells. When a water contains so much mineral or gaseous matter as to render it unfit for domestic use, it usually becomes more or less valuable for medicinal purposes. Such waters are often designated by the character of their most important medicinal constituent. Therefore we have the following varieties:

Carbonated waters, which contain carbon dioxide in considerable quantity, often holding in solution calcium and magnesium carbonates. Such waters often effervesce on coming to the surface. The Waukesha water, from Waukesha, Wisconsin, the Apollinaris, and the Marien Spring are examples of this class.

Sulphur waters contain hydrogen sulphide, and deposit sulphur on exposure to the atmosphere. Sometimes both sulphuretted hydrogen and carbon dioxide are present in the same water. Richfield Springs, New York, and White Sulphur Springs, West Virginia, belong to this class.

Alkaline waters usually contain considerable quantities of sodium bicarbonate with the sodium and magnesium sulphates. The Apollinaris water of Neuenahr, Prussia, and the Capon Springs, West Virginia, are examples of this class.

Lithia waters frequently do not contain any notable amount of mineral substance, but include small quantities of lithium carbonate or chloride. The Vichy water from Vichy, France, the Gettysburg, and the Aix-la-Chapelle are examples.

Saline waters contain relatively large proportions of magnesium and sodium sulphates with sodium chloride. The waters of Saratoga Springs, New York, and of Kissingen, Bavaria, are examples of general saline waters. Those of Carlsbad, Bohemia, and Bedford, Pennsylvania, are special magnesium waters.

Siliceous waters contain small quantities of alkaline silicates, and are represented by the hot springs of the Yellowstone Park and Iceland.

Chalybeate waters have iron as a constituent held in solution by carbon dioxide, and consequently deposit iron as a hydrate or oxide on exposure to the atmosphere. The waters of Pyrmont, Germany, Spa, Belgium, Alexisbad, Sweden, and numerous American springs belong to this class.

A number of saline waters are so rich in certain chemical compounds as to constitute an important source of these substances, notable examples being the salt-wells of Pennsylvania, Ohio, and West Virginia, whose waters furnish sodium chloride, bromine, and iodine.

4. Sea Water.—This water contains on an average 3.50 per cent. of mineral substance. Sodium chloride constitutes 2.64 per cent., and the remainder consists chiefly of magnesium chloride and sulphate and calcium sulphate. The specific gravity of sea water is 1.02721 at zero.

HYDROGEN DIOXIDE.

Formula, H_2O_2. *Molecular Weight,* 33.76.

History and Preparation.—In 1818, Thénard, on treating barium dioxide with diluted hydrochloric acid, obtained this compound according to the following reaction :

BaO_2	+	$2HCl$	=	$BaCl_2$	+	H_2O_2.
Barium Dioxide.		Hydrochloric Acid.		Barium Chloride.		Hydrogen Dioxide.

It may also be prepared by passing a stream of carbon dioxide into water, and adding barium dioxide in small quantities at a time, or, as the United States Pharmacopœia directs, by acting on hydrated barium dioxide with phosphoric acid as follows :

BaO_2	+	H_3PO_4	=	$BaHPO_4$	+	H_2O_2.
Barium Dioxide.		Phosphoric Acid.		Barium Hydrogen Orthophosphate.		Hydrogen Dioxide.

A small quantity of barium passes into solution as tetrahydrogen barium phosphate, but is afterwards precipitated with sulphuric acid.

Hydrogen dioxide for bleaching purposes may be prepared from sodium dioxide and aqueous acids. In the preparation of hydrogen dioxide on a large scale, hydrofluoric acid is employed :

$$\underset{\text{Barium Dioxide.}}{BaO_2} + \underset{\text{Hydrofluoric Acid.}}{2HF} = \underset{\text{Barium Fluoride.}}{BaF_2} + \underset{\text{Hydrogen Dioxide.}}{H_2O_2}.$$

The barium fluoride, being insoluble, is allowed to subside, and the supernatant liquid, when decanted, is ready for use. This liquid is an aqueous solution of hydrogen dioxide. It is made and sold of different strengths, according to the volume of oxygen that a certain volume of the solution will yield. That in which one volume will yield ten volumes of the gas is, perhaps, most in demand.

Solutions of hydrogen dioxide may be easily concentrated to any desirable strength by evaporation at 50° to 60° C., with but little loss up to a point where one volume of the solution will yield fifty volumes of oxygen; or they may be concentrated by freezing, as the water is easily frozen out, apparently without loss of dioxide. The anhydrous compound is obtained by concentrating the aqueous solution in a vacuum over sulphuric acid.

Properties.—Pure hydrogen dioxide is a colorless, oily liquid, with a specific gravity of 1.452. It is soluble in all proportions in ether and water. The former will extract it from its aqueous solution. Hydrogen dioxide decomposes slowly at ordinary temperatures, more rapidly at 37°, and at 100° the decomposition is explosively rapid. Solidification does not take place at —30°.

Many inert substances in powder cause decomposition into oxygen and water. The action of hydrogen dioxide is that of a strong oxidizer, since according to the following reaction it rapidly furnishes oxygen in the nascent state:

$$2H_2O_2 = 2H_2O + O_2.$$

Thus, it oxidizes sulphides to sulphates ($PbS + 4H_2O_2 = PbSO_4 + 4H_2O$), "*ous*" salts and acids to "*ic*" ($2FeSO_4 + H_2SO_4 + H_2O_2 = Fe_2(SO_4)_3 + 2H_2O$. $H_2SO_3 + H_2O_2 = H_2SO_4 + H_2O$); the alkali-earth hydroxides precipitate as peroxides. Because of the presence of a loosely combined oxygen, H_2O_2 will reduce all bodies which likewise contain such available oxygen atoms. Thus, oxides of silver, mercury, or gold are reduced to the metallic state ($Ag_2O + H_2O_2 = Ag + H_2O + O_2$); an acidified solution of potassium permanganate is reduced and decolorized ($2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$). Iodides are decomposed by strong solutions of H_2O_2 ($2KI + H_2O_2 = 2KOH + I_2$).

Aqua Hydrogenii Dioxidi, U.S.P.—This is an aqueous solution of hydrogen dioxide, containing about 3 per cent. by weight of the dioxide, which corresponds to about ten volumes of available oxygen. It is colorless and odorless; it has a slightly acidulous taste, and produces a peculiar sensation and soapy froth in the mouth. It has a specific gravity of 1.006 to 1.012 at 15° C. It is liable to deteriorate through loss of oxygen by age, exposure to heat, or protracted agitation, and various methods have been adopted for preserving it. As the decomposition is more rapid in alkaline solution, a small amount of free acid is allowed to remain in the liquid to aid in preserving it. In some cases it is preserved with boric acid and glycerin. In all cases it is best kept loosely corked in a refrigerator at from 10° to 15° C.

Uses.—On account of its oxidizing action, hydrogen dioxide is useful as a bleaching agent, for cleaning books and engravings that have become soiled by age, and for bleaching dark-colored hair. Its use in bleaching wool has become quite extensive. Cotton may be bleached by it, but not with the same ease that wool is. In medicine the use of hydrogen dioxide as an antiseptic has assumed large proportions, and used in this way in scarlet fever, diphtheria, and in many surgical operations it has been found especially valuable. For medicinal purposes the solution should be free from hydrofluoric acid and barium; and in all cases where the small proportion of the free acid present is objectionable, it may be saturated at the time the solution is to be used by a small quantity of sodium bicarbonate.

Tests.—One of the readiest methods of detecting hydrogen dioxide is by the use of a paper moistened with solutions of potassium iodide and starch. The special value of this test is that the reaction takes place in the presence of ferrous sulphate. Other oxidizing agents have the power to liberate iodine from potassium iodide, but not in the presence of ferrous sulphate. Another qualitative test consists in acidifying the solution slightly with sulphuric acid, adding ether, then a few drops of potassium chromate solution, and agitating the mixture. A blue color is developed, and, on allowing to stand, the ether separates as a deep-blue layer, the color of which is due to perchromic acid.

OXYGEN AND CHLORINE.

Three oxides and four acids of chlorine are known, as follows:

Oxides.	Acids.
Chlorine monoxide, Cl_2O.	Hypochlorous acid, $HClO$.
Chlorine trioxide, Cl_2O_3.	Chlorous acid, $HClO_2$.
Chlorine peroxide, Cl_2O_4 or $(ClO_2)_2$.	Chloric acid, $HClO_3$.
	Perchloric acid, $HClO_4$.

Chlorine and oxygen do not appear to unite directly, and the above compounds are all made by indirect methods.

It will be seen that the first two acids on the list are derived from the oxides by the addition of one molecule of water, producing two molecules of acid:

$$Cl_2O + H_2O = 2HClO.$$
$$Cl_2O_3 + H_2O = 2HClO_2.$$

No acid is formed from the peroxide, and the oxides corresponding to the two higher acids have never been isolated.

CHLORINE MONOXIDE, Cl_2O.

Preparation.—This compound is prepared by passing chlorine through concentrated sulphuric acid to dry it, and then over dry precipitated mercuric oxide, kept at a moderately low temperature:

$$\underset{\text{Mercuric Oxide.}}{2HgO} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\text{Mercuric Oxychloride.}}{Hg_2OCl_2} + \underset{\text{Chlorine Monoxide.}}{Cl_2O}.$$

The gas as formed is passed into a tube cooled by a freezing mixture, where it liquefies.

Properties.—Chlorine monoxide is a yellow gas, having an odor resembling chlorine, but not so suffocating. It is very soluble in water, 200 volumes of the gas dissolving in one volume of water. When condensed to an orange-colored liquid it boils at —19°. It is unsafe to have any quantity of it in the liquid state, since it explodes violently into its constituent elements on the slightest agitation.

HYPOCHLOROUS ACID, $HClO$.

Preparation.—This acid is formed (1) by passing chlorine monoxide into water:

$$Cl_2O + H_2O = 2HClO.$$

(2) On agitating chlorine gas with mercuric oxide and water:

HgO	+	$2Cl_2$	+	H_2O	=	$HgCl_2$	+	$2HClO$.
Mercuric Oxide.		Chlorine		Water.		Mercuric Chloride		Hypochlorous Acid

The solution is then distilled.

(3) On slowly adding a dilute mineral acid to a clear solution of bleaching powder, in just sufficient amount to decompose the hypochlorite present, hypochlorous acid is formed. A 5 per cent. solution of the acid is recommended as the best for this purpose:

$Ca(OCl)_2$	+	$2HNO_3$	=	$Ca(NO_3)_2$	+	$2HClO$.
Calcium Hypochlorite.		Nitric Acid.		Calcium Nitrate.		Hypochlorous Acid.

Properties.—The dilute acid is colorless, but when more concentrated it has a yellowish shade. When very dilute it can be distilled without decomposition. The concentrated solution is easily decomposed into chlorine, chloric acid, oxygen, and water. The acid, as well as its salts, possesses a strong oxidizing and bleaching action. Charcoal, iodine, sulphur, phosphorus, arsenic, and antimony are rapidly oxidized when brought in contact with the acid, and, if the latter be concentrated, with explosive violence, forming carbonic, iodic, sulphuric, phosphoric, arsenic, and antimonic acids. Iron filings are immediately oxidized, when brought in contact with the acid, with evolution of chlorine. Copper and mercury under similar circumstances are converted into oxychlorides.

Hypochlorites.—The sodium and calcium salts of this acid are the best known; the former is the important constituent of Labarraque's solution, and the latter of bleaching powder. This bleaching powder, or chlorinated lime, is produced in enormous quantities from the chlorine prepared from the waste hydrochloric acid of the Leblanc soda process, and is used extensively for bleaching and oxidizing, also as a ready and cheap source for chlorine in many smaller operations.

CHLORINE TRIOXIDE, CHLOROUS OXIDE, Cl_2O_3.

Preparation.—Four parts of potassium chlorate and three parts of arsenous oxide are mixed with sufficient water to form a paste; this is then warmed to 60° with a mixture of twelve parts of nitric acid (sp. gr. 1.33) and four parts of water. The reaction is best considered in two stages, as follows:

$$KClO_3 + As_2O_3 + 3HNO_3 = HClO_3 + As_2O_5 + N_2O_3 + H_2O + KNO_3.$$

Potassium Chlorate. Arsenous Oxide. Nitric Acid. Chloric Acid. Arsenic Oxide. Nitrogen Trioxide. Water. Potassium Nitrate.

$$2HClO_3 + N_2O_3 = Cl_2O_3 + 2HNO_3.$$

Chloric Acid. Nitrogen Trioxide. Chlorine Trioxide. Nitric Acid.

All methods for the preparation of this compound must be carried out with the greatest care, as a little too much heat may cause dangerous explosions.

Properties.—Chlorine trioxide is a yellowish-green gas with a very irritating odor. This gas is easily condensed to a red-brown liquid, which explodes, on the slightest provocation, with great violence.

CHLOROUS ACID, $HClO_2$.

Preparation.—This acid is formed when chlorine trioxide is passed into water:

$$Cl_2O_3 + H_2O = 2HClO_2.$$

The yellowish solution possesses weak acid properties, is unable to decompose carbonates, but combines with hydrates forming *chlorites*. These salts, as well as the acid itself, are very easily decomposed, especially in the presence of organic matter, and therefore they possess active bleaching properties.

CHLORINE PEROXIDE, Cl_2O_4.

Preparation.—Chlorine peroxide is prepared by adding powdered potassium chlorate to sulphuric acid in a retort, and after solution has taken place gently warming and collecting the heavy gas by displacement:

$$3KClO_3 + 2H_2SO_4 = KClO_4 + 2KHSO_4 + H_2O + Cl_2O_4.$$

Potassium Chlorate. Sulphuric Acid. Potassium Perchlorate. Acid Potassium Sulphate. Water. Chlorine Peroxide.

With this, as with all other compounds of chlorine and oxygen, great care must be exercised to prevent explosion. A hot wire introduced into this gas is sufficient to cause decomposition with explosive violence. When an aqueous solution of the gas is desired, a mixture of potassium chlorate and oxalic acid is heated to 70°, and the mixed chlorine peroxide and carbon dioxide which are evolved are passed into water:

$$2KClO_3 + 2H_2C_2O_4 = K_2C_2O_4 + 2H_2O + 2CO_2 + Cl_2O_4.$$

Potassium Chlorate. Oxalic Acid. Potassium Oxalate. Water. Carbon Dioxide. Chlorine Peroxide.

Properties.—Chlorine peroxide is a heavy, greenish-yellow gas, with a strong, irritating odor. On exposure to a freezing mixture it condenses to a dark-red liquid, which boils at 9° and solidifies at —79°. It is, perhaps, the most dangerous of all the oxides of chlorine, as it readily decomposes, forming one volume of chlorine and two volumes of oxygen. Many organic substances, when brought in contact with the gas, are inflamed. When dissolved in water it forms a yellow solution, which does not appear to have acid properties, since on adding an alkali to the solution a mixture of chlorite and chlorate is formed.

CHLORIC ACID, $HClO_3$.

This acid is only known in solution and in combination with certain bases as chlorates.

Preparation.—Barium chlorate is decomposed by the equivalent quantity of diluted sulphuric acid:

$$\underset{\text{Barium Chlorate.}}{Ba(ClO_3)_2} + \underset{\text{Sulphuric Acid.}}{H_2SO_4} = \underset{\text{Barium Sulphate.}}{BaSO_4} + \underset{\text{Chloric Acid.}}{2HClO_3}.$$

The clear liquid is decanted from the precipitated barium sulphate and evaporated in a vacuum over sulphuric acid. The most concentrated solution obtainable by this method contains 40 per cent. of water. On further concentration it decomposes into perchloric acid, chlorine, and oxygen, according to the following:

$$\underset{\text{Chloric Acid.}}{8HClO_3} = \underset{\text{Perchloric Acid}}{4HClO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Oxygen.}}{3O_2} + \underset{\text{Chlorine.}}{2Cl_2}.$$

Chloric acid can also be prepared by adding to potassium chlorate solution a slight excess of hydrofluosilicic acid:

$$\underset{\text{Potassium Chlorate.}}{2KClO_3} + \underset{\text{Hydrofluosilicic Acid.}}{H_2SiF_6} = \underset{\text{Potassium Hydrofluosilicate.}}{K_2SiF_6} + \underset{\text{Chloric Acid.}}{2HClO_3}.$$

The clear liquid is decanted from the insoluble potassium hydrofluosilicate, a little silica is added, and the solution evaporated, when the excess of hydrofluosilicic acid, combining with the added silica, passes off as silicon tetrafluoride, and the excess of silica settles. The solution of chloric acid may now be decanted pure. The acid containing 40 per cent. of water corresponds to the formula $HClO_3.7H_2O$.

Properties.—When of the above strength, chloric acid is a syrupy liquid, almost colorless, and of a faint chlorous odor. It

has a powerful acid reaction, and in other chemical properties resembles nitric acid. It decomposes organic matter with evolution of heat and light. Sulphur and phosphorus are inflamed on coming in contact with it.

Chlorates.—Chloric acid is monobasic, and its salts are called chlorates. The potassium and sodium salts are official under the titles **Potassii Chloras** and **Sodii Chloras**. The chlorates are all soluble in water. Potassium chlorate, which is soluble in 16.5 parts of water, is one of the most insoluble of the potassium salts, while sodium chlorate requires only 1.1 parts of water to effect solution. When a hot concentrated solution of a hydrate is saturated with chlorine the result is a chloride and a chlorate, as follows:

$$\underset{\text{Potassium Hydrate.}}{6KOH} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\text{Potassium Chloride.}}{5KCl} + \underset{\text{Potassium Chlorate.}}{KClO_3} + \underset{\text{Water.}}{3H_2O}$$

When, however, a cold dilute solution of the alkali is used, a hypochlorite is formed instead of a chlorate, according to the following reaction:

$$\underset{\text{Potassium Hydrate.}}{2KOH} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Potassium Chloride.}}{KCl} + \underset{\text{Potassium Hypochlorite.}}{KClO} + \underset{\text{Water.}}{H_2O.}$$

On the commercial scale potassium chlorate is prepared by passing chlorine into boiling milk of lime, and to this is added the proper proportion of potassium chloride, when double decomposition takes place with formation of calcium chloride and potassium chlorate. Calcium chloride is very soluble, while the less soluble potassium chlorate crystallizes out:

$$\underset{\text{Calcium Hydrate.}}{6Ca(OH)_2} + \underset{\text{Chlorine.}}{6Cl_2} = \underset{\text{Calcium Chloride.}}{5CaCl_2} + \underset{\text{Calcium Chlorate.}}{Ca(ClO_3)_2} + \underset{\text{Water.}}{6H_2O.}$$

$$\underset{\text{Calcium Chlorate.}}{Ca(ClO_3)_2} + \underset{\text{Potassium Chloride.}}{2KCl} = \underset{\text{Calcium Chloride.}}{CaCl_2} + \underset{\text{Potassium Chlorate.}}{2KClO_3.}$$

A recent improvement substitutes magnesium oxide or hydrate for lime, and, after concentrating the solution of mixed chlorate and chloride to 72° Tw., reducing the temperature to —17°. The refrigeration causes the separation of one-seventh more chlorate, and the magnesium chloride is available to be used as such, or reconverted into hydrate to be used again. The chlorates are also made now by electrolyzing potassium or sodium chlorides and allowing the nascent oxygen to act upon the hypochlorites first produced. In this case the electrolyzing cell must

be separated by a porous partition into a positive and a negative compartment, in the latter of which the chlorates form.

The chlorates melt on the application of heat, and then give off oxygen. When melted they energetically decompose such organic substances as are brought in contact with them. The dry chlorate should not be triturated with organic matter or sulphur. Such dry mixtures explode violently by percussion or rubbing, and burn brilliantly on the application of flame.

Impurities and Tests.—Chlorides, when present, are detected by giving a white precipitate with silver nitrate, soluble in ammonium hydrate and insoluble in nitric acid. Nitrates may be detected by heating the solution with zinc and potassium hydrate; in the presence of this impurity ammonia will be formed, which will turn red litmus paper blue and furnish the other evidences of its presence.

Uses.—In addition to their use in medicine, the chlorates are largely employed as an oxidizing agent in dyeing and calico-printing and in the manufacture of colored fires. In the preparation of these fireworks potassium chlorate and some organic substance, as sugar, starch, shellac, or wheat bran, are separately pulverized and then intimately mixed, avoiding friction or anything that might cause ignition or explosion. To this mixture is then added pulverized barium nitrate for green, strontium nitrate for red, sodium nitrate for yellow, and copper oxide for blue. Sulphur is sometimes an ingredient of these mixtures, but it greatly increases the risk of spontaneous combustion or explosion.

PERCHLORIC ACID, $HClO_4$.

Preparation.—Perchloric acid is produced in the decomposition of chloric acid, but this is not used as a method of preparing it. The process consists in first preparing potassium perchlorate by heating the chlorate. The latter salt, when heated to 350°, gives off a part of its oxygen and becomes a pasty mass of perchlorate and chloride.

$$2KClO_3 = KClO_4 + KCl + O_2.$$

The pasty mass is cooled, powdered, and treated with cold water to remove the potassium chloride. The undissolved residue is then digested with warm hydrochloric acid to decompose any chlorate and convert it into chloride, which is then washed out with cold water. The residue which now remains consists of nearly pure perchlorate. On heating the perchlorate in a retort with four times its weight of concentrated sulphuric acid to

110°, pure perchloric acid distils over. If the distillation be long continued, partial decomposition of the salt occurs, some water is formed, which, distilling over with the acid, causes the distillate to solidify in a crystalline mass, consisting of a hydrate with the formula $HClO_4.H_2O$. On redistilling this solid compound the pure acid first passes over at 203°, and a compound having the composition $HClO_4.2H_2O$ remains behind. This second distillation is necessary in order to get a pure acid, since in the decomposition of the first some of the sulphuric acid is liable to be carried over mechanically.

Properties.—Perchloric acid is a colorless volatile liquid, which fumes strongly on coming in contact with moist air. Its specific gravity is 1.782 at 15.5°. It dissolves in water with a hissing noise, and, when brought in contact with organic matter, causes the latter to ignite. The concentrated acid, on standing, even in the dark, rapidly decomposes, becoming dark yellow to brown in color, and finally explodes with violence. By carefully adding water until crystals form, it is converted into the hydrate, $HClO_4.H_2O$. These crystals melt at 50°, and are strongly oxidizing in their action. The diluted acid has a pure sour taste, and reddens litmus paper without bleaching it. Iron and zinc dissolve in the diluted acid, causing evolution of hydrogen.

Perchlorates.—These are nearly all quite soluble in water, and some of them are deliquescent. The potassium salt is one of the most insoluble, requiring fifty-eight parts of water to dissolve it.

Perchlorates are distinguished from the chlorates by decomposing into chlorides at a higher temperature, by remaining undecomposed on the addition of hydrochloric acid, and by not yielding ClO_2 on the addition of concentrated sulphuric acid. From chlorides they are distinguished by giving no precipitate with silver nitrate, and from both nitrates and chlorates by not decolorizing indigo solution on the addition of hydrochloric acid.

OXYGEN AND BROMINE.

Unlike chlorine, bromine appears to form no stable compounds with oxygen; the following acids, however, show a similarity between the oxygen compounds of these two halogen elements:

Hypobromous acid,	$HBrO$.
Bromic acid,	$HBrO_3$.
Perbromic acid,	$HBrO_4$.

HYPOBROMOUS ACID, HBrO.

Preparation.—This compound is prepared by agitating a mixture of mercuric oxide, water, and bromine, when the following reaction takes place:

$$\underset{\text{Mercuric Oxide.}}{2HgO} + \underset{\text{Bromine.}}{2Br_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Hypobromous Acid.}}{2HBrO} + \underset{\text{Mercuric Oxybromide.}}{Hg_2OBr_2}.$$

By successive additions of bromine and mercuric oxide, a solution may be obtained containing 6.2 per cent. of the acid. This solution decomposes under ordinary circumstances on heating, but in a vacuum it may be distilled unchanged at 40°.

Properties.—The aqueous acid has a yellow color, and is an active oxidizing and bleaching agent.

BROMIC ACID, $HBrO_3$.

Preparation.—Bromic acid is prepared by first obtaining a bromate from bromine and a hydrate:

$$\underset{\text{Bromine.}}{3Br_2} + \underset{\text{Potassium Hydrate.}}{6KOH} = \underset{\text{Potassium Bromide.}}{5KBr} + \underset{\text{Potassium Bromate.}}{KBrO_3} + \underset{\text{Water.}}{3H_2O}.$$

The bromate being less soluble than the bromide is easily separated from it by crystallization. It is converted into the barium bromate, which is then decomposed with sulphuric acid.

Properties.—The nearly colorless acid solution cannot be concentrated by heat, since it decomposes at 100° into bromine and oxygen; but by evaporating at ordinary temperatures in a vacuum over sulphuric acid it may be reduced to a strength corresponding to the formula $HBrO_3.7H_2O$. Further concentration even at ordinary temperatures causes decomposition. In many of its properties it closely resembles chloric acid.

The bromates are generally soluble in water, and are decomposed on heating. Some give off oxygen with formation of bromides, while others evolve both bromine and oxygen, leaving an oxide of the metal.

Perbromic acid, $HBrO_4$, is said to have been discovered, but subsequent investigators have failed to confirm this.

OXYGEN AND IODINE.

One oxide and two acids of these elements are known, as follows:

Oxide.	Acids.
Iodine pentoxide, I_2O_5.	Iodic acid, HIO_3.
	Periodic acid, HIO_4.

IODINE PENTOXIDE, I_2O_5.

Preparation.—One part of iodine is heated with ten parts of pure concentrated nitric acid until complete solution takes place and there are no more fumes evolved. On evaporating until a temperature of 200° is attained, all the nitric acid is removed and a white residue remains.

IODIC ACID, HIO_3.

Preparation.—The simplest method of preparation is by dissolving the above oxide in water:

$$I_2O_5 + H_2O = 2HIO_3.$$

It may also be prepared from barium iodate and sulphuric acid. The iodate is made by dissolving powdered iodine in hot concentrated solution of potassium chlorate, and adding a few drops of nitric acid. After the evolution of chlorine has ceased and the solution has become cool, crystals of potassium iodate separate out. On dissolving this salt in water and adding barium chloride, barium iodate separates out as a white solid. This is then decomposed by the careful addition of sulphuric acid.

Iodic acid is also formed when chlorine is passed into water in which finely-powdered iodine is suspended:

I_2	+	$5Cl_2$	+	$6H_2O$	=	$2HIO_3$	+	$10HCl$.
Iodine.		Chlorine.		Water.		Iodic Acid.		Hydrochloric Acid.

The hydrochloric acid is removed by moist, freshly-precipitated silver oxide.

Properties.—Iodic acid occurs in the form of colorless, rhombic crystals, having a specific gravity of 4.629 at 0°. It is very soluble in water, but insoluble in alcohol. On heating to 170° the acid decomposes into iodine pentoxide and water. Organic matter, phosphorus, and sulphur inflame on coming into contact with the acid. Sulphurous oxide, sulphuretted hydrogen, and hydriodic acid decompose it with liberation of iodine.

The iodates are mostly soluble in water. On heating, some of them decompose into oxygen and an iodide, while others give off both oxygen and iodine, a metallic oxide remaining. The iodates are detected by adding to the solution a small quantity of sulphurous acid or a sulphate, to liberate iodine, and then a dilute solution of starch, with which the latter forms a blue color.

PERIODIC ACID, HIO_4.

Preparation.—This acid is only known in the free state with two molecules of water. It is obtained most readily by acting on perchloric acid with iodine:

$2HClO_4$	+	I_2	+	$2H_2O$	=	$2HIO_4.2H_2O$	+	Cl_2.
Perchloric Acid.		Iodine.		Water.		Periodic Acid.		Chlorine.

Properties.—This compound consists of colorless, transparent crystals, which are deliquescent and readily soluble in water. They melt at 133° to 140°, and on the further increase of heat are decomposed into iodine pentoxide, water, and oxygen.

SULPHUR.

Symbol, S. *Atomic Weight*, 31.83. *Valence*, II.

Sulphur was known to the ancients.

Occurrence.—It occurs in the free state, mixed with earthy matter, in the vicinity of extinct as well as active volcanoes. Its existence in the free state is supposed to be due to the sulphur dioxide and hydrogen sulphide in volcanic gases, which, reacting on each other, form sulphur, as follows:

$$SO_2 + 2H_2S = 2H_2O + S_3.$$

In combination sulphur is found, as sulphide, combined with iron, lead, zinc, copper, mercury, and some other metals in smaller amount; as sulphate, combined with calcium in gypsum, with barium in heavy spar, with magnesium in kieserite, and with sodium and potassium. Sulphur also exists in the vegetable and animal kingdoms, combined in various organic compounds, and in some mineral waters as hydrogen sulphide.

Source.—The principal source of sulphur has always been the volcanic districts in the island of Sicily and the other volcanic regions that border the Mediterranean.

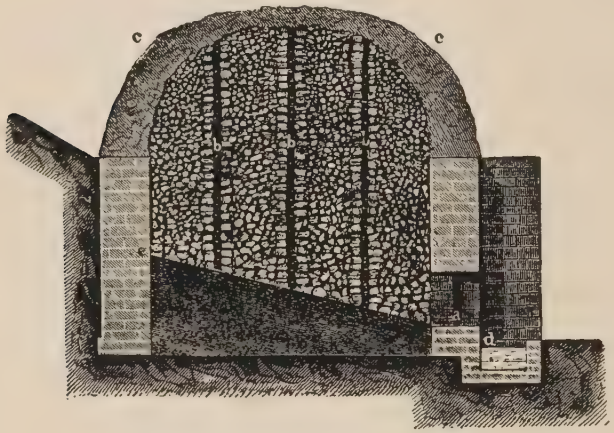
In recent years very large deposits have been found in the United States. A large mine is worked near Santa Barbara, in California. Two hundred miles south of Salt Lake City, at Cove Springs, Utah, a deposit of sulphur exists two thousand feet square and of unknown depth; shafts have been sunk to the depth of sixty feet without reaching the bottom. This sulphur is free from antimony and arsenic. The annual output in Utah and Nevada amounts to several hundred tons. The cost of transportation is the greatest obstacle to our obtaining all our sulphur from these sources. The exportation from Sicily amounts to about 400,000 tons annually. The production in the United States amounted in 1897 to 1690 tons. Utah and Louisiana produced nearly all of this. There were used 210,000 tons of imported pyrites, containing 43 per cent. of sulphur, and 119,000 tons of American pyrites, containing 44 per cent. of sulphur.

In addition to the above sources, sulphur is found in Iceland, Mexico, Central America, and the Sandwich Islands. Volcanoes in all these places either are or have been the cause of the deposit. In Mexico the sulphur is hoisted in buckets from the crater of Popocatapetl.

Extraction and Purification.—The sulphur earth and masses of ore are piled, with a small amount of fuel, in heaps over depressions in the earth. The heaps are then ignited; the sulphur melts, runs down, and is collected from the hollow beneath.

Only about one-third of the sulphur is saved by this means, the other two-thirds being consumed in heating. This process has been modified from time to time, so as to decrease the loss. One of these modifications, shown in Fig. 106, consists of a furnace of mason-work, with an inclined bottom. When the ore is filled in, a number of channels are left to assist in the distribution

FIG. 106.



Extraction of sulphur.

of the heat, and over the top of all is placed a layer of powdered ore and then a layer of the burnt ore. The pile is then ignited at the bottom of the furnace, and the sulphur running down the inclined bottom is removed at the mouth. The principal advantages of this process arise from the increased size of the furnace and the closed bottom, which enables one to control the operation, so that less sulphur is burned. Some of these furnaces are as much as 10 meters in diameter, and several weeks are required to complete one charge. The richest ores, containing 30 to 40 per cent. of sulphur, yield as much as 25 per cent., and the poorer ones, containing 20 to 25 per cent., yield 10 to 15 per cent.

More recently a method has been introduced in which the ore is placed in a perforated basket and then immersed in solution

of calcium chloride of such strength that its boiling point is higher than that at which sulphur melts, 114.5°. Under these conditions the sulphur melts out from its ore, and sinks to the bottom of the tank, where it is drawn off in a comparatively pure form.

The alkali waste in the Leblanc soda process consists of calcium sulphide. This product, before removal from the leaching vats, is subjected to a current of air by which the sulphide is partly converted into sulphite and thiosulphate. The mixture is then treated with hydrochloric acid, when the following reaction takes place:

$$\underset{\text{Calcium Sulphide.}}{2CaS} + \underset{\text{Calcium Thiosulphate.}}{CaS_2O_3} + \underset{\text{Hydrochloric Acid.}}{6HCl} = \underset{\text{Calcium Chloride.}}{3CaCl_2} + \underset{\text{Sulphur.}}{4S} + \underset{\text{Water.}}{3H_2O}.$$

A newer and as it seems more satisfactory process is that of Chance. The alkali waste is first decomposed according to the reactions:

$$2CaS + CO_2 + H_2O = CaCO_3 + Ca(SH)_2 \text{ and}$$
$$Ca(SH)_2 + CO_2 + H_2O = CaCO_3 + 2H_2S.$$

The hydrogen sulphide gas, mixed with air, is then passed over oxide of iron at a low red heat, when the hydrogen burns with separation of sulphur:

$$H_2S + O = H_2O + S.$$

In England the sulphur is recovered from the purifiers in the gas-works. The gas, which contains hydrogen sulphide, is passed over moist ferric hydrate, when the following reaction takes place:

$$\underset{\text{Ferric Hydrate.}}{Fe_2(OH)_6} + \underset{\text{Hydrogen Sulphide.}}{3H_2S} = \underset{\text{Ferrous Sulphide.}}{2FeS} + \underset{\text{Sulphur.}}{S} + \underset{\text{Water.}}{6H_2O}.$$

The mass is then exposed to the air, by which sulphur is deposited, and the hydrate regenerated, as follows:

$$\underset{\text{Ferrous Sulphide.}}{2FeS} + \underset{\text{Water.}}{3H_2O} + \underset{\text{Oxygen.}}{3O} = \underset{\text{Ferric Hydrate.}}{Fe_2(OH)_6} + \underset{\text{Sulphur.}}{S_2}.$$

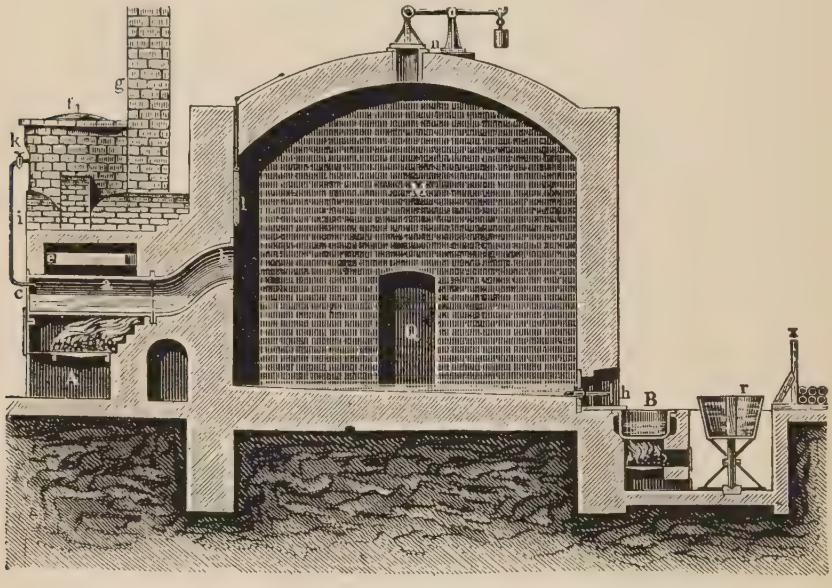
The hydrate, mixed with sulphur, is then exposed to another quantity of the gas, and again regenerated until the mass contains 50 per cent. of sulphur; the latter is then recovered by heating the mixture.

In France, Germany, and Sweden, sulphur is largely obtained by distilling iron pyrites; such sulphur is liable to contain considerable quantities of arsenic.

The crude sulphur, as obtained by the various processes just described, contains 2 or 3 per cent. of impurities. To remove these the process of sublimation is resorted to. A furnace similar to that in Fig. 107 is employed. The crude sulphur is melted in the vessel K, with the waste heat from the furnace; it is then run in small quantities at a time into the retort *a*, from which it sublimes into the large chamber M. At first, while the chamber is cool, the sulphur is deposited in fine powder, but as the whole becomes heated it melts and is run off at the bottom into moulds, and becomes the roll sulphur or brimstone of commerce.

Properties.—Sulphur is a lemon-yellow, crystalline solid, odorless, and almost without taste. It is insoluble in water, almost insoluble in alcohol, ether, and volatile oils, but easily

FIG. 107.



Sublimation of sulphur.

soluble in fixed oils. Its specific gravity at 0° is 2.05. On the application of heat sulphur melts at 114.5°, and remains liquid until cooled to 111°. The liquid is straw-yellow at first, but becomes dark red and viscid on gradually raising the temperature from 200° to 250°, when it is too thick to pour, and becomes almost black in color. A further increase of temperature causes

the sulphur to become thin in consistence, but it remains dark in color, and at 448.4° it boils under ordinary pressure.

Sulphur, as above described, exists in the form of rhombic octahedra, that being the form in which it occurs in nature, as well as that in which it forms from solution in carbon disulphide. When, however, certain conditions are complied with, sulphur may easily be obtained in several allotropic modifications. On heating it in a Hessian crucible until melted, allowing to cool until a crust forms on the surface, and then quickly pouring out the liquid portion, the crucible will be lined with long, brilliant, transparent crystals, having the form of monoclinic prisms ; these become opaque after twenty-four hours at ordinary temperature, and are then found to be made up of minute rhombic crystals. Monoclinic sulphur has a specific gravity of 1.96, melts at 120°, and is soluble in carbon disulphide.

Another modification may be prepared by carefully heating sulphur to 330°, and then pouring in a thin stream into water. The product in this case is an amber-colored, elastic mass, which may be drawn out into threads or kneaded between the fingers. This is called the plastic variety. It has a specific gravity of 1.957, and is insoluble in carbon disulphide. At 100° it quickly reverts to the rhombic variety with evolution of heat, hence no melting point can be assigned to it.

An insoluble variety similar to this is formed when hydrochloric acid is added to calcium pentasulphide. Small quantities of this insoluble variety are also frequently found in sublimed sulphur.

On heating sulphur in the air to about 230° it inflames, combining with the oxygen of the air to form sulphur dioxide. In the presence of air and moisture the finely-divided sulphur is slowly oxidized at ordinary temperatures, forming sulphurous and sulphuric acids.

Sulphur combines directly with many other non-metals, as hydrogen, chlorine, bromine, iodine, and phosphorus, and with most metals.

SULPHUR AND HYDROGEN.

HYDROGEN SULPHIDE.

SULPHURETTED HYDROGEN.

Formula, H_2S. *Molecular Weight,* 33.83.

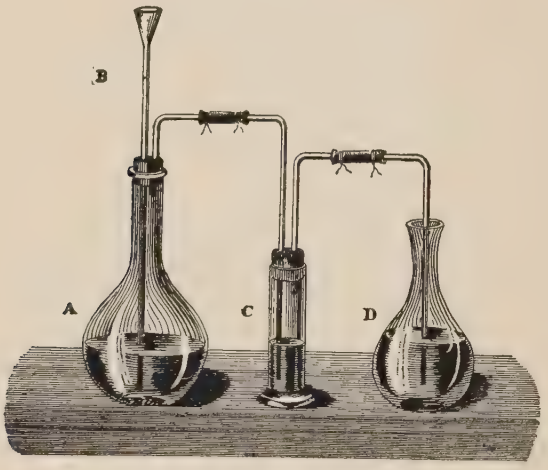
History.—Hydrogen sulphide was noticed by the ancients, but Scheele, in 1777, was the first to investigate it by heating sulphur with hydrogen.

Occurrence.—It occurs in nature when organic bodies containing sulphur putrefy, in volcanic gases, and in many mineral waters. The sulphur waters in Virginia are the most important in the United States.

Preparation.—Hydrogen sulphide is formed when a stream of hydrogen is passed over sulphur heated to the boiling point.

For all practical purposes, however, an apparatus similar to that illustrated in Fig. 108 answers the purpose most satisfactorily.

FIG. 108.



Preparation of hydrogen sulphide.

In the generator, A, is placed some ferrous sulphide, and to it is added sulphuric acid, previously diluted with six volumes of water, when the following reaction takes place.

$$\underset{\text{Ferrous Sulphide.}}{FeS} + \underset{\text{Sulphuric Acid.}}{H_2SO_4} = \underset{\text{Ferrous Sulphate.}}{FeSO_4} + \underset{\text{Hydrogen Sulphide.}}{H_2S}.$$

The gas is readily evolved without the application of heat, and may either be used directly or passed through a little water in the wash-bottle at C. When it is desired to prepare the solution of the gas it is passed into water in the flask D.

Ferrous sulphide frequently contains metallic iron, in which case the gas will contain some free hydrogen. This is rarely an objection, but, if it should be, then a pure gas may be obtained by treating antimonous sulphide with hydrochloric acid:

$$\underset{\text{Antimonous Sulphide.}}{Sb_2S_3} + \underset{\text{Hydrochloric Acid.}}{6HCl} = \underset{\text{Antimonous Chloride.}}{2SbCl_3} + \underset{\text{Hydrogen Sulphide.}}{3H_2S.}$$

The gas may also be prepared by heating in a flask a mixture of paraffin and sulphur; a number of other organic substances may be used in place of the paraffin.

Properties.—Hydrogen sulphide is a colorless gas with a disagreeable odor and a sweetish taste. Its density is 16.99. One volume of water dissolves 4.37 volumes of the gas at 0°, and 3.23 volumes at 15°.

The solution reddens litmus, and rapidly undergoes change on exposure to air, water and sulphur being the result, the latter separating out. Under a pressure of 17 atmospheres the gas condenses to a liquid, which solidifies at −85°.

Hydrogen sulphide is a very inflammable gas, burning with a pale blue flame. The products of its combustion are water and sulphur dioxide, or, if the combustion is rapid, sulphur.

The gas is decomposed by many oxidizing agents; chlorine, for example, changes it immediately, according to the reaction:

$$H_2S + Cl_2 = 2HCl + S.$$

A similar reaction takes place with bromine and with iodine; in the latter case, however, the reaction is possible only in the presence of water.

Sulphuretted hydrogen, owing to the readiness with which it parts with its sulphur, forms an active reducing agent. Thus,—

$$\underset{\text{Ferric Chloride.}}{Fe_2Cl_6} + H_2S = \underset{\text{Ferrous Chloride.}}{2FeCl_2} + 2HCl + S.$$

$$\underset{\text{Arsenic Oxide.}}{As_2O_5} + 2H_2S = \underset{\text{Arsenous Oxide.}}{As_2O_3} + 2H_2O + S_2.$$

$$\underset{\text{Chromium Trioxide.}}{2CrO_3} + 3H_2S = \underset{\text{Chromium Sesquioxide.}}{Cr_2O_3} + 3H_2O + S_3.$$

Hydrogen sulphide combines with many metals, decomposing their oxides, hydrates, or carbonates. Many of the metallic sulphides possess characteristic colors. This fact adds to the value of the gas or its solution in chemical analysis.

The solution has also been used medicinally; it is given internally in about one-half ounce doses.

The Sulphides.—Many of these compounds occur native, and after a proper purification are ready for use. When, however, it is desired to prepare a sulphide, it is usually accomplished by heating together sulphur and the metal, or by passing hydrogen sulphide into a solution of the metallic chloride. In some cases an alkali is necessary in order to neutralize the free acid

formed; in other cases the precipitation takes place best in hydrochloric acid solution.

HYDROGEN PERSULPHIDE, H_2S_2.

This compound, which is the counterpart of hydrogen dioxide, exists in the form of a yellow oily liquid. It is prepared by boiling together 1 part of slaked lime, 6 parts of water, and 2 parts of sublimed sulphur, and pouring the clear solution into cold concentrated hydrochloric acid. The heavy, yellowish, oily compound separates and sinks to the bottom. It possesses an odor similar to that of hydrogen sulphide, and an acrid, unpleasant taste. It readily decomposes into hydrogen sulphide and sulphur. The most interesting feature of this compound is its combination with strychnine, forming a beautiful compound, having the formula $2C_{21}H_{22}N_2O_2 + 3H_2S_2$.

SULPHUR AND CHLORINE.

These elements combine directly to form three distinct compounds.

Sulphur Monochloride, S_2Cl_2, is formed by passing dry chlorine over dry sulphur. A reddish-yellow liquid is formed, which may be rectified by distillation. It has a specific gravity of 1.705, and boils at 138°. It is a solvent of sulphur to the extent of 66 per cent., forming a thick syrupy liquid which is used in vulcanizing rubber.

Sulphur Dichloride, SCl_2, is formed when dry chlorine is passed into the monochloride at 0°. The excess of chlorine is removed by passing carbon dioxide through the liquid. The dichloride is an unstable, dark-red liquid, slowly decomposing at ordinary temperatures into the monochloride and chlorine. The same decomposition takes place on the addition of water.

Sulphur Tetrachloride, SCl_4, is prepared by passing chlorine into the dichloride at a temperature of —20° to —22°. This is a mobile, yellowish-brown liquid, which decomposes as the temperature rises from —20°. On the addition of water the decomposition takes place with explosive rapidity.

SULPHUR AND BROMINE.

Bromine Monosulphide, S_2Br_2, is the only compound of these two elements known at the present time. It is prepared by the direct union of the elements, the excess of bromine being removed by carbon dioxide. It is a heavy, red liquid, which is stable at ordinary temperatures, but decomposes slowly at the boiling point, 200° to 210°, into sulphur and bromine.

SULPHUR AND IODINE.

These two elements unite in two proportions.

Sulphur Moniodide, S_2I_2, is formed when the two elements are heated together under water, or, according to the Pharmacopœia, without water in a loosely-stoppered flask. They are directed to be first thoroughly mixed and then gently heated until the mass becomes of a uniform, dark color, when the temperature is increased to the point necessary to melt

them. After cooling, the grayish-black mass is rubbed to powder. Thus prepared **Sulphuris Iodidum**, U. S. P., is a grayish-black, crystalline solid, with the characteristic odor of iodine, having a somewhat acrid taste and a slightly acid reaction. It is insoluble in water, soluble in sixty parts of glycerin, and very soluble in carbon disulphide. Alcohol and ether remove the iodine, leaving the sulphur. It is gradually decomposed on exposure to the air with loss of iodine. On the application of heat it melts at 60°, and at a higher temperature sublimes with partial decomposition, without leaving any residue. Prolonged boiling with water removes the iodine, which escapes with the steam, leaving the sulphur.

Sulphur Hexiodide, SI_6, is obtained by evaporating a solution of the two elements in carbon disulphide, when crystals similar to those of iodine separate.

SULPHUR AND OXYGEN.

The following compounds of these two elements are known:

Sulphur sesquioxide, S_2O_3.
Sulphur dioxide, SO_2.
Sulphur trioxide, SO_3.
Sulphur heptoxide, S_2O_7.

Three of these, SO_2, SO_3, and S_2O_7, unite with water to form corresponding acids, the first and second being the more important.

$SO_2 + H_2O = H_2SO_3$, Sulphurous acid.
$SO_3 + H_2O = H_2SO_4$, Sulphuric acid.
$S_2O_7 + H_2O = H_2S_2O_8$, Persulphuric acid.

There are also the following acids, the oxides corresponding to which have not been discovered:

H_2SO_2, Hyposulphurous acid.
$H_2S_2O_3$, Thiosulphuric acid.
$H_2S_2O_6$, Dithionic acid.
$H_2S_3O_6$, Trithionic acid.
$H_2S_4O_6$, Tetrathionic acid.
$H_2S_5O_6$, Pentathionic acid.

SULPHUR SESQUIOXIDE, S_2O_3.

This compound is formed when sulphur is added, in small quantity at a time, to sulphur trioxide. It separates as a dark-blue liquid, which solidifies into bluish-green, crystalline crusts:

$$SO_3 + S = S_2O_3.$$

It readily decomposes into sulphur dioxide and sulphur:

$$2S_2O_3 = 3SO_2 + S.$$

HYPOSULPHUROUS ACID, H_2SO_2.

This compound was called hydrosulphurous acid by Schützenberger, its discoverer. The above title, however, is more in accordance with its constitution. It should not be confounded with *thiosulphuric acid*, which is sometimes improperly called hyposulphurous acid.

Preparation.—When zinc is added to sulphurous acid the following reaction takes place:

$$\underset{\text{Zinc.}}{Zn} + \underset{\text{Sulphurous Acid.}}{H_2SO_3} = \underset{\text{Zinc Sulphite.}}{ZnSO_3} + \underset{\text{Hydrogen.}}{H_2}.$$

$$\underset{\text{Sulphurous Acid.}}{H_2SO_3} + \underset{\text{Hydrogen}}{H_2} = \underset{\text{Hyposulphurous Acid.}}{H_2SO_2} + \underset{\text{Water.}}{H_2O}.$$

Properties.—This is a yellow liquid with powerful reducing properties. On exposure to air it is rapidly decomposed, as follows:

$$\underset{\text{Hyposulphurous Acid}}{2H_2SO_2} = \underset{\text{Sulphur Dioxide.}}{SO_2} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Sulphur.}}{S}.$$

It is a more powerful bleaching agent than sulphurous acid, and precipitates a number of the metals from solutions of their salts, for example:

$$\underset{\text{Mercuric Chloride.}}{HgCl_2} + \underset{\text{Hyposulphurous Acid.}}{H_2SO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Mercury.}}{Hg} + \underset{\text{Hydrochloric Acid.}}{2HCl} + \underset{\text{Sulphurous Acid.}}{H_2SO_3}.$$

This serves to distinguish it from sulphurous acid. Salts of this acid have been formed, which are true hyposulphites. When sodium bisulphite is treated with zinc, the mixture kept cool, and air excluded, the hyposulphite is formed according to the following reaction:

$$\underset{\text{Sodium Bisulphite}}{3NaHSO_3} + \underset{\text{Zinc.}}{Zn} = \underset{\text{Acid Sodium Hyposulphite.}}{NaHSO_2} + \underset{\text{Sodium Sulphite.}}{Na_2SO_3} + \underset{\text{Zinc Sulphite.}}{ZnSO_3} + \underset{\text{Water.}}{H_2O}.$$

The zinc and sodium sulphites crystallize out as a double salt, the solution is mixed with four times its volume of strong alcohol, by which the remainder of this salt is removed, and the solution is set aside, when crystals of the hyposulphite separate. These should be dried in a vacuum.

SULPHUR DIOXIDE

Formula, SO_2. *Molecular Weight*, 63.59.

History.—Sulphur dioxide, or sulphurous oxide, was readily recognized by the ancients, since it is always formed when sulphur is burned in the air.

Occurrence.—It occurs native as a volcanic gas, and is found in small quantity in the air of large cities, on account of the existence of sulphur in coal.

Preparation.—(1) When sulphur is burned in air or oxygen,

direct union of the elements takes place with the formation of sulphur dioxide :

$$S_2 + 2O_2 = 2SO_2.$$

This process of burning is used for nearly all cases where the gas is made on a large scale, as in bleaching and the manufacture of sulphites and sulphuric acid.

(2) When three parts of sulphur are mixed with four parts of manganese dioxide, and the mixture is heated, sulphur dioxide is given off :

S_2	+	MnO_2	=	MnS	+	SO_2
Sulphur.		Manganese Dioxide.		Manganous Sulphide.		Sulphur Dioxide.

(3) On a smaller scale for laboratory purposes, copper turnings in a glass flask are covered with strong sulphuric acid and the mixture heated gradually, so as to maintain a steady effervescence. Mercury and silver give the same result. Some sulphide is formed at the same time, but the reaction is practically as follows :

Cu	+	$2H_2SO_4$	=	$CuSO_4$	+	$2H_2O$	+	SO_2.
Copper.		Sulphuric Acid.		Copper Sulphate.		Water.		Sulphur Dioxide.

(4) When the copper in the above reaction is replaced by charcoal, the gas is evolved according to the following :

C	+	$2H_2SO_4$	=	$2H_2O$	+	CO_2	+	$2SO_2$.
Carbon		Sulphuric Acid.		Water.		Carbon Dioxide.		Sulphur Dioxide.

This method is not available when the gas is required absolutely pure, on account of the accompanying carbon dioxide, but for making the official **Acidum Sulphurosum** the small quantity of carbonic acid is no disadvantage.

(5) Sulphur and sulphuric acid heated together give the pure gas :

$$S + 2H_2SO_4 = 2H_2O + 3SO_2.$$

(6) When warm diluted sulphuric acid is added to a sulphite, the gas is given off freely :

Na_2SO_3	+	H_2SO_4	=	Na_2SO_4	+	H_2O	+	SO_2.
Sodium Sulphite.		Sulphuric Acid.		Sodium Sulphate		Water.		Sulphur Dioxide.

Properties.—Sulphur dioxide is a colorless gas, having a suffocating odor. One volume of water at 0° dissolves 79.8 volumes, and at 20° 39.4 volumes of the gas. When water at 0° is saturated with the gas, it deposits crystals having the

formula $H_2SO_3.14H_2O$. These crystals melt at 1° to 2°, without evolution of the gas. At a temperature of —10°, or under a pressure of three atmospheres, the gas condenses to a colorless, mobile liquid, which boils at —8°, and at —76° becomes a crystalline solid.

The liquid sulphur dioxide has a specific gravity of 1.49 at 20.5°. It is manufactured by Pictet, of Geneva, and sent into commerce in copper cylinders. On the large scale, pressure affords the cheapest means of converting the gas into the liquid state, but for laboratory experiments it may be readily obtained in the liquid condition by passing it through a tube surrounded by a freezing mixture of salt and ice. The liquid may also be prepared and preserved by sealing in a strong glass tube one part of sulphur and five parts of sulphur trioxide. The reaction takes place spontaneously according to the following :

$$2SO_3 + S = 3SO_2.$$

A low temperature may be produced by the vaporization of liquid sulphur dioxide, and this may be intensified by directing a current of air over its surface.

The gas is very stable under high temperatures until 1200° are attained, when decomposition into sulphur trioxide and sulphur takes place :

$$3SO_2 = 2SO_3 + S.$$

Both gaseous and liquid sulphur dioxide, in the presence of water, possess active bleaching properties. The action in this case is a *reducing* one, the opposite to that by which chlorine accomplishes the same purpose. In the presence of organic matter it appears to have the power of decomposing water, combining with the oxygen, while the hydrogen in the nascent state is free to combine with the oxygen of the coloring matter, forming colorless compounds :

$$SO_2 + 2H_2O = H_2SO_4 + H_2.$$

The coloring matter is not destroyed, as in the case of chlorine, but may be restored by neutralizing with an alkali, hence the importance of thorough washing to remove these sulphur compounds in the process of bleaching. It is especially valuable in the bleaching of wool and silk where chlorine would injure the fabric.

With solutions of the metallic hydrates and carbonates, sulphur dioxide produces sulphites according to the following reactions :

$2KOH$	+	SO_2	=	K_2SO_3	+	H_2O
Potassium Hydrate		Sulphur Dioxide.		Potassium Sulphite		Water
K_2CO_3	+	SO_2	=	K_2SO_3	+	CO_2
Potassium Carbonate.		Sulphur Dioxide.		Potassium Sulphite.		Carbon Dioxide.

Certain metallic peroxides are converted by sulphur dioxide into sulphates, as follows:

PbO_2	+	SO_2	=	$PbSO_4$.
Lead Peroxide.		Sulphur Dioxide.		Lead Sulphate.

Iodine is converted into hydriodic acid by sulphur dioxide:

I_2	+	SO_2	+	$2H_2O$	=	H_2SO_4	+	$2HI$.
Iodine.		Sulphur Dioxide.		Water		Sulphuric Acid.		Hydriodic Acid.

In the absence of water this reaction is reversed, as follows:

$$H_2SO_4 + 2HI = I_2 + SO_2 + 2H_2O.$$

Sulphur dioxide is detected by paper which has been saturated with solutions of potassium iodate and starch. When this is brought in contact with the gas the starch is turned blue by the liberated iodine, as follows:

$2KIO_3$	+	$5SO_2$	+	$4H_2O$	=	$2KHSO_4$	+	$3H_2SO_4$	+	I_2
Potassium Iodate.		Sulphur Dioxide.		Water.		Acid Potassium Sulphate.		Sulphuric Acid		Iodine

If, however, the gas should be in excess it will react on the free iodine, according to the reaction given above for the formation of hydriodic acid, and the paper will be bleached.

Uses.—The gas is used extensively in bleaching, disinfecting, and in the manufacture of sulphurous acid and the sulphites. The cheapest source is from sulphur or iron pyrites. Its antiseptic properties are especially valuable for the preservation of meat.

SULPHUROUS ACID.

Formula, H_2SO_3 *Molecular Weight*, 81.47.

Acidum Sulphurosum, U. S. P.—This acid is not known in the free state, but there are good reasons for believing that it exists in aqueous solution.

Preparation.—It is prepared by passing sulphur dioxide into water at 10°. The United States Pharmacopœia recommends that the gas be prepared from sulphuric acid and charcoal, but on a larger scale it is generally made by burning sulphur. For the details and reactions involved in the preparation of the gas, the preceding pages on sulphur dioxide may be consulted.

Properties.—The official sulphurous acid is a colorless liquid, of a sulphurous odor, and an acid, sulphurous, and somewhat astringent taste. It has the specific gravity 1.035 at 15°, and contains 6.4 per cent. of the gas by weight. It reddens litmus paper strongly, and then bleaches it. On the application of heat, all the gas is given off, and then the water volatilizes, leaving no residue. This property would serve to detect many impurities. Not more than a turbidity should be produced on adding to sulphurous acid a little barium chloride and dilute hydrochloric acid, indicating the absence of more than traces of sulphuric acid.

Sulphites.—Sulphurous acid is dibasic, that is, has two hydrogen atoms replaceable by bases. This gives rise to two series of salts, the *acid* or *bi*-sulphites, in which only one hydrogen atom is replaced, as follows :

$$\underset{\text{Potassium Hydrate.}}{KOH} + \underset{\text{Sulphurous Acid.}}{H_2SO_3} = \underset{\text{Potassium Bisulphite.}}{KHSO_3} + \underset{\text{Water.}}{H_2O},$$

and the *normal* sulphites, in which both hydrogen atoms are replaced, as follows :

$$\underset{\text{Potassium Hydrate.}}{2KOH} + \underset{\text{Sulphurous Acid.}}{H_2SO_3} = \underset{\text{Potassium Sulphite.}}{K_2SO_3} + \underset{\text{Water}}{2H_2O}.$$

The sulphites are usually prepared by passing the gas from burning sulphur into a solution of a hydrate ; the amount of gas used determines whether an acid or normal sulphite is formed. Except the sulphites of the alkali metals, they are rather insoluble in water.

Heat decomposes most of the sulphites, some into oxides and sulphur dioxide, as :

$$CaSO_3 = CaO + SO_2,$$

others into sulphates and sulphides, as :

$$4K_2SO_3 = 3K_2SO_4 + K_2S.$$

They are also decomposed on the addition of hydrochloric or sulphuric acid, evolving sulphur dioxide, and forming a chloride or sulphate of the base. The sulphite of potassium, $K_2SO_3.2H_2O$, and the bisulphite and sulphite of sodium, $NaHSO_3$ and $Na_2SO_3.7H_2O$, are official.

Detection.—The sulphites, as well as the bisulphites, are easily detected by the addition of zinc and hydrochloric acid, when hydrogen sulphide will be evolved :

$$3Zn + 6HCl + H_2SO_3 = 3ZnCl_2 + 3H_2O + H_2S.$$

The use of free hydrochloric acid is necessary, since in its absence the following reaction takes place :

$$Zn + 2H_2SO_3 = ZnSO_3 + H_2SO_2 + H_2O.$$

The salts of silver, mercury, and lead added to sulphurous acid or a sulphite produce a precipitate which blackens on heating, owing to formation of sulphide.

The sulphites and bisulphites are largely used in bleaching and disinfecting, and in addition are employed more or less in medicine.

PRACTICAL EXERCISES.

(1) In a flask, similar to that arranged for the preparation of chlorine, place a few copper turnings and cover them with concentrated sulphuric acid. Apply a gentle heat, gradually increasing until effervescence commences, and collect the resulting gas by downward displacement, as under chlorine. This gas is sulphurous oxide.

(2) A dry tube full of the gas inverted in a vessel of water will show the ready solubility of it in that liquid.

(3) A piece of moistened blue litmus paper held in the gas will at first become red, but after the lapse of some time will turn white, thus showing the bleaching property of the gas.

(4) Plunge a lighted taper into a tube full of the gas ; it is quickly extinguished, indicating that the gas is neither combustible nor a supporter of combustion.

(5) Pass the gas into water until the latter smells strongly of it, then add to the resulting liquid a solution of potassium permanganate ; the purple color of the latter will be destroyed as rapidly as added.

SULPHUR TRIOXIDE.

Sulphuric Oxide.

Formula, SO_3. *Molecular Weight*, 79.47.

Preparation.—This compound may be prepared by direct union of two volumes of sulphur dioxide with one volume of oxygen, by the aid of red-hot platinum sponge :

$$2SO_2 + O_2 = 2SO_3.$$

The white fuming compound is conducted into a well-cooled receiver where it condenses in long needles. It is important that all parts of the apparatus be free from moisture, and that the gases be previously well dried by passing them through sulphuric acid, and then through a column of pumice, moistened with the concentrated acid. This method has been so modified as to make it available for working on a large scale, by allowing concentrated

sulphuric acid to fall drop by drop on pieces of red-hot bricks, when the following decomposition takes place :

$$2H_2SO_4 = 2SO_2 + O_2 + 2H_2O.$$

This mixture is freed from moisture by passing it through sulphuric acid, by which the H_2O is removed, and the remaining SO_2 and O passed over red-hot spongy platinum, to combine them into sulphuric oxide. When the fuming, or Nordhausen, sulphuric acid is carefully heated in a glass or platinum retort, sulphuric oxide distils, leaving ordinary sulphuric acid behind :

$$H_2S_2O_7 = H_2SO_4 + SO_3.$$

On heating concentrated sulphuric acid with phosphorus pentoxide, water is extracted and sulphuric oxide formed :

$$H_2SO_4 + P_2O_5 = 2HPO_3 + SO_3.$$

Properties.—Sulphur trioxide consists of long transparent prisms. When perfectly anhydrous it fuses at 14.8°, and boils at 46.2°. On standing for some time at ordinary temperatures, long crystalline fibres slowly form, which fuse at 50°. This has been termed a second modification of sulphur trioxide ; it is readily converted into the first by fusing and then reducing the temperature to 14°. At the present time it is considered that there is but one form of the trioxide, the fibrous modification melting at 50° being produced by the absorption of traces of moisture.

The pure trioxide when melted has a specific gravity of 1.97 at 20°. Sulphur trioxide possesses a great affinity for water and fumes on exposure to air. When thrown on water it dissolves with a hissing noise :

$$SO_3 + H_2O = H_2SO_4.$$

When mixed with barium oxide the following reaction takes place :

$$\underset{\text{Barium Oxide.}}{BaO} + \underset{\text{Sulphur Trioxide.}}{SO_3} = \underset{\text{Barium Sulphate.}}{BaSO_4}.$$

The evolution of heat is so great in this reaction that the mass becomes red-hot. Sulphur trioxide is manufactured on a large scale, and comes into commerce in soldered iron boxes or sealed glass globes.

Uses.—It is used in the preparation of artificial alizarin, and in dissolving indigo, having replaced to a certain extent the Nordhausen sulphuric acid.

SULPHURIC ACID.

Formula, H_2SO_4. *Molecular Weight*, 97.35.

History.—Geber, in the eighth century, appears to have prepared this acid in an impure state, but the first exact knowledge dates from the fifteenth century, when Basil Valentine prepared it by distilling ferrous sulphate. A crude form of the present process is said to have been introduced into England, from the Continent, in the early part of the last century, by Cornelius Drebbel. This method consisted in burning sulphur and nitre together in large glass globes, the bottoms of which were covered with water. This glass vessel was replaced by the present lead chamber, at the suggestion of Dr. Roebuck, in 1746.

Occurrence.—In the free state sulphuric acid is found in springs originating in the vicinity of volcanoes, and in certain rivers that have their sources in the Andes of South America. In combination it occurs as the sulphates of calcium, barium, magnesium, and a number of other metals.

Preparation.—The formation of sulphuric acid is based on the oxidation of sulphur dioxide in the presence of water. This takes place slowly by atmospheric oxygen, but rapidly by the oxides of nitrogen, which in turn readily take oxygen from the atmosphere.

The following reaction is the simplest expression for what takes place in the "lead chamber process:"

$$\underset{\text{Sulphur Dioxide.}}{2SO_2} + \underset{\text{Nitrogen Tetroxide.}}{N_2O_4} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Sulphuric Acid.}}{2H_2SO_4} + \underset{\text{Nitrogen Dioxide.}}{N_2O_2}.$$

This reaction may be accomplished on a small scale by conducting into a large glass globe sulphur dioxide, nitrogen dioxide, steam, and air. The process will apparently go on indefinitely, since the nitrogen dioxide is reconverted into tetroxide by the oxygen of the air; but the nitrogen of the air is present in increasing amount, and so dilutes the mixture as to prevent further action until it is removed.

When the steam is not simultaneously admitted with the others there are deposited "lead chamber crystals," nitrosyl-sulphuric acid:

$$2SO_2 + N_2O_4 + O + H_2O = 2HSO_3NO_2,$$

which dissolve on the admission of steam, forming sulphuric acid and red fumes:

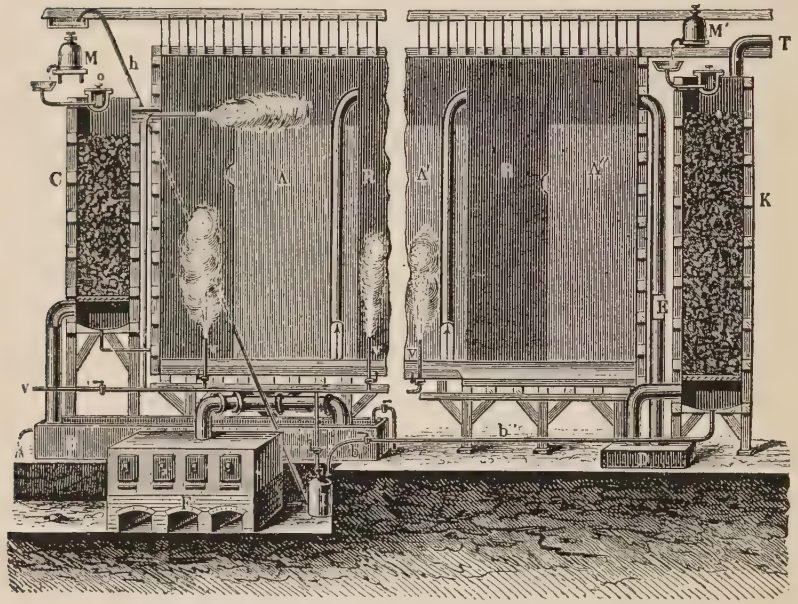
$$2HSO_3NO_2 + H_2O = 2H_2SO_4 + N_2O_3.$$

On the large scale the lead chamber process is carried out by the most economical methods, and therefore by the use of the cheapest materials. In England the sulphur dioxide is prepared by roasting pyrites, FeS_2; in the United States from pyrites, and by burning sulphur. The oxides of nitrogen are prepared by the action of sulphuric acid on Chili saltpetre.

A view of the lead chambers with the two towers is shown in Fig. 109.

The details of the process are, briefly, as follows: Sulphur

FIG. 109.



Preparation of sulphuric acid.

dioxide, generated by one of the methods above stated, is passed into the Glover tower, C, where it is cooled and mixed with dilute sulphuric acid which trickles down over the pieces of bricks into the tower from M; at the same time from an adjoining cistern there runs down, and mixes with this, concentrated sulphuric acid containing oxides of nitrogen in solution.

The effect of this mixing with dilute acid is to liberate the oxides of nitrogen from the concentrated acid, which oxides, with

sulphur dioxide, oxygen, nitric acid, and steam, are passed into chamber A, where the following reactions take place:

$$(1)\ SO_2 + 2HNO_3 = H_2SO_4 + N_2O_4.$$
$$(2)\ 2N_2O_3SO_2 + O_2 + 2H_2O = 2H_2SO_4 + 2N_2O_3.$$

From the first chamber the uncombined gases pass into a second chamber where further combination and condensation take place, and in a third chamber the condensation is completed so that only oxides of nitrogen and nitrogen gas escape into the Gay-Lussac tower, K. In this latter tower the oxides are dissolved by concentrated sulphuric acid from M, trickling down over pieces of coke.

When this concentrated acid reaches the bottom, saturated with oxides of nitrogen, it is transferred by suitable pipes to the top of the Glover tower to run down and mix with fresh quantities of dilute acid and sulphur dioxide. The concentrated acid for the Gay-Lussac tower is taken from the bottom of the Glover tower, as the mixed dilute and strong acids in meeting with the hot gases have been deprived of nearly all water.

The circulation of gases through the system of towers and chambers is maintained by the draught of a tall chimney.

It will be seen that the same sulphuric acid is repeatedly used and nearly all the oxides of nitrogen are saved, so that the process consists in generating a continuous supply of sulphur dioxide with a small quantity of nitric acid to make up the loss which is unavoidable. The principal supply of oxygen comes from the atmosphere.

The furnace in which the sulphur or pyrites is burned is so arranged as to furnish the necessary heat for the decomposition of the nitrate.

The acid in the bottom of the lead chamber is drawn off when it attains a specific gravity of 1.55 to 1.60,—containing 64 per cent. of absolute sulphuric acid. If allowed to become more concentrated than this it begins to absorb nitrous fumes. It is then concentrated in leaden pans until it reaches the specific gravity of 1.75, containing 78 per cent. of the acid, when it commences to attack the lead, and is, therefore, transferred to vessels of iron, glass, or, best of all, platinum, to be finally concentrated or distilled. Even platinum is slowly attacked by the acid, so that recently it has been found advantageous to line these platinum stills with gold.

The lead chamber process has been carried to the highest

development in England, where the annual production of the acid is nearly one million tons.

Theoretically 100 parts of sulphur should yield 305.9 parts of sulphuric acid, but in practice this is never quite reached. 290 parts are about the average, and in some of the best works 297 parts are attained.

The amount of sodium nitrate required also varies. In manufactories where both the Gay-Lussac and Glover towers are used, only 3.5 to 7.5 parts of the nitre are found necessary for every 100 parts of sulphur.

Sulphuric acid, when prepared without distillation, is dark in color and contains lead sulphate, arsenic, and nitrogen trioxide. The arsenic may be removed by adding a small quantity of hydrochloric acid and boiling, when arsenous chloride will pass off; the nitrogen trioxide may be removed by the addition of ammonium sulphate, when the following reaction takes place with evolution of nitrogen :

$$(NH_4)_2SO_4 + N_2O_3 = H_2SO_4 + 3H_2O + 2N_2.$$

Finally, to remove lead and any other fixed impurities, the acid is distilled from glass or gold-lined platinum retorts. When one-third of the acid has passed over, the receiver is changed and the remainder, distilled nearly to dryness, furnishes the pure, colorless acid.

Properties.—When pure, sulphuric acid is a colorless, oily, inodorous, corrosive liquid of the specific gravity 1.840, and containing not less than 96 per cent. of absolute H_2SO_4. When all but 2 per cent. of water has been removed and the acid cooled, crystals of pure H_2SO_4 separate out, which melt at 10.5°. These crystals, when melted, will frequently retain the liquid condition considerably below the solidifying point; when, however, the liquid is agitated, or a crystal is added, the mass solidifies, and the temperature rises to 10.5°. The pure liquid has the specific gravity 1.854 at 0°, and 1.834 at 24°, compared with water at the same temperatures.

Acidum Sulphuricum, U. S. P., has a specific gravity of 1.835 at 15°, and contains 92.5 per cent. by weight of absolute H_2SO_4. On heating the absolute acid it begins to fume at 30°, sulphur trioxide escaping. This evolution of the trioxide continues until the temperature reaches 338°, and is maintained at that, when a liquid distils over unchanged containing 98.4 to 98.8 per cent of H_2SO_4. On diluting with water until the acid

has the specific gravity 1.78 and the composition $H_2SO_4 + H_2O$, the so-called monohydrated acid crystallizes at 0°, and the crystals melt at 7.5°.

Sulphuric acid has a strong affinity for water, and when mixed with it great heat is developed. In diluting, the acid should always be poured into the water, slowly and with constant stirring; when the reverse is attempted the acid is liable to be thrown out by the violent ebullition resulting from the sudden rise in temperature. The mixing is accompanied by diminution of volume, the maximum contraction amounting to 8 per cent. when one molecule of the acid is mixed with two of water. On account of this affinity for water, organic substances are rapidly decomposed, hydrogen and oxygen in the proportion to form water being removed, and carbon, in many compounds, separating out. An example of this occurs when sulphuric acid is added to sugar. The concentrated acid does not so readily attack metals as that which is more diluted. In some cases the metal becomes coated with a layer of sulphate, which prevents further action. This is notably the case with zinc and iron. Copper, mercury, antimony, bismuth, lead, and silver are dissolved on heating with the acid, a reduction of the latter taking place with an evolution of sulphur dioxide at the same time. Gold, platinum, and some other of the noble metals are not appreciably affected even by boiling with the acid. For this reason the latter when concentrated may be used to separate silver from gold.

Uses.—Sulphuric acid is consumed in all branches of chemical industry. Perhaps its most extensive use is in the Leblanc soda industry, where the chamber acid is employed without concentration. It is also largely consumed in the refining of petroleum, in the manufacture of fertilizers, in making parchment, in the conversion of starch into glucose, and in the manufacture of carbon dioxide from calcium carbonate.

Tests and Impurities.—Sulphuric acid and sulphates are detected by giving a white precipitate with barium chloride, insoluble in hot concentrated acids; also by the white precipitate which they form with salts of lead, insoluble in dilute acids, but soluble in hot concentrated acids. Sulphates may also be detected by heating a fragment on charcoal with sodium carbonate and moistening the fused mass on a silver coin with a drop of diluted hydrochloric acid, when a dark stain of silver sulphide will be produced. This is known as the *Hepar* reaction.

Sulphuric acid is liable to contain lead, nitric acid, or nitrogen trioxide, arsenic, selenium, and organic matter. It should volatilize from a glass or platinum dish at a temperature of 350° without residue. Lead is detected on diluting with water, or, better, with alcohol, when a precipitate of lead sulphate will take place. When some of the acid in a test-tube is covered with a layer of ferrous sulphate solution, no dark ring should be formed at the point of contact of the two liquids, indicating the absence of *nitric acid* and the *oxides of nitrogen*. When considerably diluted with water and treated with pure zinc it evolves a gas which should not blacken paper moistened with solution of silver nitrate, indicating the absence of *arsenic* or *sulphurous acid*.

When the acid is mixed with twice its volume of water, the mixture added to half its bulk of sulphurous acid, and then allowed to stand, no red color of separated selenium should occur, according to the following reaction :

$$\underset{\text{Selenous Acid.}}{H_2SeO_3} + \underset{\text{Sulphurous Acid.}}{2SO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Sulphuric Acid.}}{2H_2SO_4} + \underset{\text{Selenium.}}{Se.}$$

Organic matter is recognized by the dark color it imparts to the acid.

Sulphates.—Sulphuric acid forms two series of salts, the *neutral* or *normal* sulphates, in which both hydrogen atoms of the acid are replaced by a base, as Na_2SO_4, and the *acid* sulphates, in which only one hydrogen atom is replaced by a base, as $NaHSO_4$. Most of the sulphates are soluble in water, the important exceptions being those of barium, strontium, calcium, and lead. The sulphates of sodium, ammonium, iron, and certain alkaloids have extensive use in medicine.

NORDHAUSEN OR DISULPHURIC ACID, $H_2S_2O_7$.

This is the oldest of the sulphuric acids, and was originally manufactured in the vicinity of Nordhausen, Germany, by the distillation of dried ferrous sulphate in earthen retorts :

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3.$$

There is also a small quantity of water necessarily present, since ferrous sulphate retains one molecule of water until decomposition begins ; therefore a weak acid is first formed which carries with it most of the sulphur dioxide, and should be rejected. The distillate is saved when the white fumes of the trioxide make their appearance. There is still enough moisture present to make a liquid acid of a composition corresponding to the above formula.

At the present time most of the acid is made in Bohemia. The operation is commenced by roasting pyrites, by which ferrous sulphate and basic ferric sulphate, $Fe_2S_2O_9$, are formed. On lixiviating the mass a solution of the sulphates is obtained, which, on evaporation and ignition, gives a residue of the basic sulphate alone. The presence of the ferrous salt is avoided as far as possible on account of the formation of sulphur dioxide as above given. On submitting the basic salt to distillation the following reaction takes place:

$$Fe_2S_2O_9 = Fe_2O_3 + 2SO_3.$$

The residue is the *caput mortuum* or *colcothar* used in polishing. The acid is also prepared by dissolving sulphur trioxide in concentrated sulphuric acid:

$$H_2SO_4 + SO_3 = H_2S_2O_7.$$

This would require about 45 per cent. of the trioxide, but the commercial acid often contains less than 20 per cent. of it.

Properties.—Fuming sulphuric acid is a thick, oily liquid, colorless when pure, but often of a brownish color from small quantities of organic matter. As ordinarily found, its specific gravity is rarely above 1.865. Since the introduction of the trioxide into commerce the liquid may be obtained in sealed tubes or bulbs. It is of semi-solid consistence, and of the specific gravity 1.900. When the acid is cooled, large crystals separate, which are of a white color and melt at 35°.

Disulphuric acid forms both acid and normal salts; for example, with sodium we have $NaHS_2O_7$ and $Na_2S_2O_7$.

The Nordhausen acid has not any use in pharmacy, but is employed largely in the arts for dissolving indigo and in the preparation of artificial alizarin.

THIOSULPHURIC ACID, $H_2S_2O_3$.

This acid is not known in the free state, but only in combination in certain salts, of which sodium thiosulphate, $Na_2S_2O_3.5H_2O$, is the most important. The salt is improperly called hyposulphite of sodium, and consequently the acid is also miscalled hyposulphurous acid, a name which belongs to the compound H_2SO_2.

Preparation.—The sodium salt is prepared by boiling together sulphur and sodium sulphite:

$$Na_2SO_3 + S = Na_2S_2O_3.$$

It is also formed when sulphur dioxide is passed into a solution

of sodium sulphide, the reaction taking place in two stages according to the following:

$$(1)\ 3SO_2 + 2Na_2S = 2Na_2SO_3 + 3S.$$
$$(2)\ Na_2SO_3 + S = Na_2S_2O_3.$$

On adding iodine to a solution of sodium sulphide and sulphite, the thiosulphate is formed as follows:

$$Na_2S + Na_2SO_3 + I_2 = Na_2S_2O_3 + 2NaI.$$

When sodium, or calcium, pentasulphide is exposed to the air, it absorbs oxygen and is converted into thiosulphate:

$$Na_2S_5 + 3O = Na_2S_2O_3 + 3S.$$

In case the calcium salt is formed, it may be converted into the sodium salt by the addition of sodium carbonate. The lime used in purifying illuminating gas, and known as *gas lime*, contains calcium pentasulphide and hyposulphite. This is exposed to the air, whereby the sulphide is converted into thiosulphate, the mass is lixivated with water, and the solution, by double decomposition with sodium carbonate, gives calcium carbonate and sodium thiosulphate, as follows:

$$CaS_2O_3 + Na_2CO_3 = CaCO_3 + Na_2S_2O_3.$$

This and the *ball soda*, the waste from the manufacture of sodium carbonate, are the sources of the commercial salt.

Properties.—Sodium thiosulphate occurs in large, colorless, transparent, monoclinic prisms or plates, efflorescent in dry air, odorless, having a cooling, somewhat bitter and sulphurous taste, and a neutral or faintly alkaline reaction. It is soluble in 1.5 parts of water at 15°, and in 0.5 part of boiling water, in the latter case with partial decomposition. When rapidly heated it melts at 50°, and at 100° loses all its water (36.26 per cent.).

The aqueous solution dissolves the halogen salts of silver, the reaction being,—

$$\underset{\text{Silver Chloride.}}{AgCl} + \underset{\text{Sodium Thiosulphate.}}{Na_2S_2O_3} = \underset{\text{Sodium-silver Thiosulphate.}}{NaAgS_2O_3} + NaCl.$$

This reaction takes place in "fixing" dry plates after development.

Solutions of iodine are decolorized by this salt according to the following equation:

$$I_2 + 2Na_2S_2O_3 = 2NaI + \underset{\text{Sodium Tetrathionate.}}{Na_2S_4O_6}.$$

When a solution of thiosulphate is treated with an acid, sulphur dioxide is given off and sulphur is precipitated:

$$Na_2S_2O_3 + 2HCl = 2NaCl + SO_2 + S + H_2O.$$

This reaction serves to distinguish the thiosulphates from the sulphites.

PERSULPHURIC ACID, $H_2S_2O_8$.

Potassium and ammonium persulphates may be prepared by electrolyzing acid solutions of potassium or ammonium sulphates respectively. The crystalline persulphates separate at the positive pole or anode of the battery.

The most striking property of the persulphates is their powerful oxidizing action, whether used in neutral, acid, or alkaline solution. From chlorides, bromides, and iodides the free halogen is liberated, while a neutral sulphate is formed, ferrocyanides are changed into ferricyanides, manganates in alkaline solution are changed into permanganates, and many of the metals are dissolved with the formation of sulphates. Many organic substances are also oxidized by acid or alkaline persulphate solutions. Thus, indigo, litmus, and turmeric are easily bleached by it.

DITHIONIC ACID, $H_2S_2O_6$.

Preparation.—When sulphur dioxide is passed into water in which manganese dioxide is suspended, the following reaction takes place:

$$MnO_2 + 2SO_2 = MnS_2O_6.$$

Dithionic acid is also formed when a dilute solution of iodine in potassium iodide is added to a solution of acid sodium sulphite:

$$2NaHSO_3 + I_2 = H_2S_2O_6 + 2NaI.$$

The dithionates are not so easily oxidized as the thiosulphates. On heating, however, they are decomposed into sulphur dioxide and sulphite. They do not precipitate sulphur on the addition of hydrochloric acid and heating; this distinguishes them from the thiosulphates.

TRITHIONIC ACID, $H_2S_3O_6$.

Preparation.—When sublimed sulphur and a strong solution of acid potassium sulphite are digested at a temperature of from 50° to 60°, the potassium salt of trithionic acid is formed, as follows:

$$6KHSO_3 + S_2 = 2K_2S_3O_6 + K_2S_2O_3 + 3H_2O.$$

When a concentrated solution of potassium thiosulphate is saturated with sulphur dioxide, potassium trithionate is formed:

$$2K_2S_2O_3 + 3SO_2 = 2K_2S_3O_6 + S.$$

On adding iodine to a solution of sodium thiosulphate and sulphite, sodium trithionate is produced:

$$Na_2S_2O_3 + Na_2SO_3 + I_2 = Na_2S_3O_6 + 2NaI.$$

When the potassium salt, obtained in the second method, is treated with hydrofluosilicic acid the free acid is produced:

$$K_2S_3O_6 + SiF_4.2HF = H_2S_3O_6 + SiF_4.2KF.$$

This diluted acid allows of only moderate concentration in a vacuum, for it readily decomposes into sulphur, sulphur dioxide, and sulphuric acid. The potassium salt is the only one which is well known.

TETRATHIONIC ACID, $H_2S_4O_6$.

Preparation.—The sodium salt of this acid is formed when iodine is added to an aqueous solution of sodium thiosulphate:

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$$

The free acid may be prepared by carefully decomposing barium tetrathionate with diluted sulphuric acid. The diluted acid may be boiled, but on concentrating decomposition takes place, as follows:

$$H_2S_4O_6 = H_2SO_4 + SO_2 + S_2.$$

PENTATHIONIC ACID.

When hydrogen sulphide is passed into a solution of sulphur dioxide, pentathionic acid results, with separation of sulphur:

$$5H_2S + 5SO_2 = H_2S_5O_6 + 4H_2O + 5S.$$

The solution is milky, and is best cleared by digesting with metallic copper. Any copper which is dissolved is precipitated by hydrogen sulphide.

SELENIUM.

Symbol, Se. *Atomic Weight*, 78.6. *Valence*, II.

History.—Selenium was discovered in 1817 by Berzelius, in the deposits from sulphuric acid chambers, and named from σελήνη, the moon.

Occurrence.—It is widely distributed in small quantities associated with sulphur and in iron pyrites.

Preparation.—This element is most conveniently prepared from lead chamber deposits. The crude material is mixed with sufficient sulphuric acid to make a paste, heated to the boiling point, and treated with nitric acid from time to time, until the red color disappears. The solution, which now contains selenic acid, H_2SeO_4, is, when cold, poured off from the sediment and saturated with sulphur dioxide, when selenium separates out as a red powder.

Thus prepared it contains lead, and sometimes other metals, from which it may be purified by distillation or by fusing with potassium nitrate and sodium carbonate, forming sodium selenate, from which it is precipitated as a red powder by hydrochloric acid.

Another method is to evaporate the solution of selenic acid, obtained as above, to remove nitric acid, and then boil with con-

centrated hydrochloric acid, by which the selenic acid is reduced to selenous acid, as follows :

$$H_2SeO_4 + 2HCl = Cl_2 + H_2O + H_2SeO_3.$$

The solution containing selenous acid is then saturated with sulphur dioxide, when selenium separates out according to the following reaction :

$$H_2SeO_3 + 2SO_2 + H_2O = 2H_2SO_4 + Se.$$

Selenium may also be prepared by digesting the lead chamber deposit on a water bath with a concentrated solution of potassium cyanide :

$$KCN + Se = SeKCN.$$

From this solution the selenium is deposited, in red flakes, on the addition of hydrochloric acid. The residue may be purified by distillation, or by fusion as previously described.

Properties.—Like sulphur, selenium exists in different allotropic modifications.

(1) The amorphous form, soluble in carbon disulphide.

This variety is obtained by quickly cooling the molten selenium. It exists as an amorphous, nearly black mass, of the specific gravity 4.28.

(2) From the solution of the above amorphous variety in carbon disulphide dark-red, monoclinic crystals separate. These crystals have a specific gravity of 4.5, and are isomorphous with the monoclinic crystals of sulphur.

(3) When the amorphous variety is warmed for some time at 97°, it is converted into a lead-gray, crystalline mass, which is insoluble in carbon disulphide and has the specific gravity of 4.5.

(4) If a concentrated solution of sodium or potassium selenide be exposed to the air for some time, black microscopic crystals of metallic selenium separate, which have a specific gravity of 4.8. The first and second varieties change at from 90° to 100° into the third, and the second, third, and fourth, when melted and quickly cooled, change to the first. The varieties which dissolve in carbon disulphide soften and melt so slowly that no constant melting point can be assigned to them. The insoluble varieties melt at 117°. All the different forms boil at about 700°, forming a reddish-yellow vapor, which may be condensed in scarlet powder. Like sulphur, the vapor density of selenium decreases as the temperature rises. At 1400° it possesses the normal density corresponding to the formula Se_2.

When heated in the air, selenium burns with a bright blue flame, yielding selenium dioxide, SeO_2. The vapor has an odor resembling horse-radish.

The compounds of selenium are very similar to those of sulphur. Hydrogen selenide is a very irritating, disagreeably smelling gas. One oxygen compound, SeO_2, and two acids, selenous and selenic, are known. Selenic acid, H_2SeO_4, corresponding to sulphuric acid, H_2SO_4, resembles the latter in many respects, but has one characteristic property not possessed by any other acid, namely, that of dissolving gold,—the selenic being reduced to selenous acid at the same time.

The compounds of selenium are best detected by the red precipitate of the element which occurs on the addition of sulphurous acid or sulphur dioxide.

TELLURIUM.

Symbol, Te. *Atomic Weight*, 126.5. *Valence*, II.

History.—Tellurium was discovered in 1782 by Müller von Reichenstein, and more fully investigated by Klaproth and Berzelius. It was named tellurium by Klaproth from *tellus*, the earth.

Occurrence.—This element occurs sparingly in the free state, and as tellurides of gold, silver, lead, bismuth, and mercury in California, Colorado, Brazil, and Hungary.

Preparation.—Bismuth telluride is fused with sodium carbonate. The resulting telluride of sodium, still mixed with a small quantity of sulphide, is dissolved in water and exposed to the air, by which the metal is precipitated. It is then purified by distillation in a stream of hydrogen.

Properties.—Tellurium is a silver-white metal of a brittle texture, and has a specific gravity of 6.24. It melts at about 500°, and volatilizes at about 1300°, yielding yellow vapors. It is insoluble in carbon disulphide, but dissolves in concentrated sulphuric acid, imparting a deep-red color to the solution, from which it is precipitated on the addition of water.

On heating in the air, it burns with a blue flame, yielding white fumes of tellurium dioxide.

Tellurium compounds are recognized by fusing with potassium carbonate, by which potassium telluride is formed, which dissolves in water with a red color, and, on the addition of hydrochloric acid, yields the disagreeably smelling compound, hydrogen telluride.

CHAPTER V.

THE NITROGEN GROUP.

NITROGEN.

Symbol, N. *Atomic Weight*, 13.93. *Valence*, III.

History.—The fact that something existed in the atmosphere which would not support life appears to have been observed in 1772 by Dr. Rutherford, Professor of Botany in the University of Edinburgh. He confirmed the correctness of his observation by treating the air which had been breathed by animals with potassium hydrate to remove carbon dioxide, and then found that the residue would not support life or combustion. In consequence of this he is usually given the credit of having discovered the element. About the same time the composition of air was investigated by Priestley, Scheele, Lavoisier, and Chaptal. The last suggested the present name, from νίτρον, nitre, and γενναω, I produce, since it was found to be a constituent of saltpetre. Lavoisier suggested the name *azote*, which is still retained by the French, with the symbol Az, the symbol N being used by all other nations.

Occurrence.—In the free state nitrogen constitutes four-fifths of the atmosphere. In combination with sodium and oxygen, it occurs in enormous quantities as Chili saltpetre. Animal and vegetable substances always contain a distinct quantity of it.

Preparation.—(1) Nitrogen may be prepared by removing the oxygen from the air. This is accomplished by attaching a porcelain crucible or crucible lid to a cork so that the two will float on water. The phosphorus is placed on the porcelain, ignited, and a bell-jar immediately brought over the whole, so as to rest with its rim below the surface of the water. The phosphorus is extinguished so soon as the oxygen is all consumed, and after cooling the water rises and fills one-fifth the volume of the jar. The remaining four-fifths are nearly pure nitrogen. The white fumes given off during the combustion are phosphorus pentoxide, and are rapidly dissolved by the water. The residue on the crucible lid consists of some uncombined phosphorus with phosphorus trioxide.

(2) Nitrogen may also be prepared by removing the oxygen

from the atmosphere with red-hot copper. The copper is heated to redness in a glass or porcelain tube, and air, previously purified by passing it over sulphuric acid and potassium hydrate to remove organic impurities, moisture, and carbon dioxide, is passed over it; almost pure nitrogen results, which may be collected over mercury, or over water if a very little moisture be no objection.

(3) When chlorine is passed into solution of ammonium hydrate, nitrogen is evolved:

$$8NH_3 + 3Cl_2 = 6NH_4Cl + N_2.$$

It is very important to keep the ammonia in excess, for, should the amount of chlorine exceed that of ammonia, the dangerously explosive nitrogen chloride will form. This process is not to be recommended when we have so many safer and simpler ones.

(4) Solutions of ammonium nitrate and ammonium chloride heated together evolve both chlorine and nitrogen, according to the following reaction:

$$4NH_4NO_3 + 2NH_4Cl = 5N_2 + Cl_2 + 12H_2O.$$

The chlorine may be removed by passing the resulting mixed gases through sodium hydrate solution or milk of lime,

(5) Ammonium dichromate when heated evolves nitrogen:

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2.$$

The ammonium dichromate for the above method is formed when potassium dichromate and ammonium chloride are heated together, and is immediately decomposed. The whole reaction may be expressed as follows:

$$K_2Cr_2O_7 + 2NH_4Cl = Cr_2O_3 + 2KCl + 4H_2O + N_2.$$

(6) A similar method consists in heating ammonium nitrite:

$$NH_4NO_2 = 2H_2O + N_2.$$

The ammonium salt in this, as in the preceding, case is decomposed at the moment of its formation, in this method the cheaper and more available materials being potassium nitrite and ammonium chloride:

$$KNO_2 + NH_4Cl = KCl + N_2 + 2H_2O.$$

The gas may be evolved from the dry salts, but it comes off with greater regularity when they are previously dissolved in a little water.

Properties.—Nitrogen is a colorless, tasteless, and inodorous gas. Its density is 14.01, making it a trifle lighter than air. It is

very slightly soluble in water, 100 volumes of the liquid absorbing 1.5 volumes of the gas at 12 66° ; it is somewhat more soluble in alcohol.

Under a pressure of 35 atmospheres and a temperature of —146° nitrogen liquefies. In this liquid state it has a specific gravity of 0.885, boils at —194.4, and solidifies at —214°.

Nitrogen is neither combustible nor a supporter of combustion. In the free state it is remarkably inactive toward all other elements ; but its compounds, which are always formed by indirect means, are in nearly all cases very active ; many of them, the alkaloids and cyanides, for example, being especially active physiologically.

Uses.—Nitrogen is useful in carrying out such chemical operations as require the exclusion of oxygen.

THE ATMOSPHERE.

History.—Air was considered one of the elements by the ancients, but this idea was broken down when oxygen was discovered by Priestley and nitrogen by Rutherford, over a century ago ; and the relation of these two elements to the atmosphere was investigated by Lavoisier and Cavendish.

Distribution.—Air exists at the surface of the earth and to an unknown height above it. It is estimated by some to be a layer forty-five miles and by others two hundred miles in thickness.

On account of its being an elastic body it will be denser at the sea-level ; consequently we must consider it to be at a height of forty-five miles a gas of extreme tenuity. The time during which twilight is visible in the zenith has given the basis on which the calculation of forty-five miles has been made ; but it has been observed that meteors ignite at a distance of about two hundred miles above the earth's surface, thus rendering it probable that there is some resistance at that height.

Weight.—Pure dry air is 14.42 times heavier than hydrogen, consequently one liter at 0° and 760 millimeters pressure weighs 1.2917 gramme. The pressure of the atmosphere at the sea-level is, therefore, very nearly fifteen pounds on every square inch of surface, equal to a column of mercury at 0°, 760 millimeters in height. This pressure rapidly diminishes as we ascend from the sea-level.

Argon.—Argon was discovered in 1895 by Lord Rayleigh and Professor William Ramsay, in the atmosphere, of which it constitutes about 1 per cent. They did not succeed in combining

it with other elements, and therefore gave it the name *argon*, which signifies "no energy." It is a colorless gas, and is either an elementary substance or a mixture which is extremely difficult to resolve. It has been assigned the symbol A and the atomic weight 40. The molecule and atom of argon are identical. Argon is about two and a half times as soluble in water as nitrogen. It has been liquefied at —186.9° C., and solidifies at —189.6° C. Argon has been found dissolved in a few mineral waters, and some rare earths yield it on heating. Later investigations assure us of the elementary nature of this gas.

Helium.—Helium, which is analogous to argon, was first discovered in a terrestrial source in 1895 by Professor William Ramsay, upon heating certain minerals *in vacuo* and collecting the gases which were given off. It is a colorless gas, which is very sparingly soluble in water and remarkably inert. Its atomic weight is 4 and its molecule is monatomic.

Neon, Metargon, Krypton, Xenon.—Through a systematic fractionation of liquefied argon, Professor Ramsay discovered, in addition to helium, minute quantities of several other gaseous elements, which he named Neon, Metargon, Krypton, and Xenon. This latter occurs to the extent of 4 cubic centimeters in 600,000 liters of air. According to their provisional densities and atomic weights they form a group as follows :

	Helium.	Neon.	Argon.	Krypton.	Xenon.
Density (H = 1) . . .	1.98	10	19.96	40.8	64
Atomic weight	4	20	40 .	81.6	128

Composition.—The atmosphere is made up of seventy-nine volumes of nitrogen and twenty-one volumes of oxygen. There are always present small quantities of water, carbon dioxide, argon, ammonium carbonate and nitrate, sodium chloride, and particles of floating matter generally known as dust. By weight the proportion is 77 per cent. of nitrogen and 23 per cent. of oxygen. The proportion of carbon dioxide is variable, being on an average 0.03 per cent., but is found in cities often as high as 0.11 per cent. The amount of aqueous vapor is still more variable, and is affected by local causes, as temperature and altitude; the average is estimated at about 0.75 per cent. All the great number of analyses made of air during the past fifty years, by many different investigators, show but slight variations from the figures above given, although the samples have been taken from all parts of the globe and from

elevations of fourteen thousand feet. The constancy of these proportions led some of the earlier chemists to believe that air was a compound of oxygen and nitrogen, but in view of certain properties we must conclude that it is a mechanical mixture.

Properties.—The following are some of the characters which prove it to be a mixture :

(1) The physical and chemical properties of a mixture of seventy-nine volumes of nitrogen and twenty-one volumes of oxygen are exactly the same as air. When the two gases are mixed there is no evidence of chemical action, the temperature of the mixture remaining the same as that of the constituents.

(2) The proportion in which the two elements exist in air bears no relation to their atomic weights, and this proportion has been found to vary beyond the reasonable error of analysis, while a chemical compound does not vary in the proportion of its constituents.

(3) When air is drawn through a thin layer of caoutchouc, that which passes through is composed of about forty-two volumes of oxygen and fifty-eight volumes of nitrogen, on account of the property that oxygen has of passing through this medium more rapidly than nitrogen.

(4) On agitating air with water until the latter is saturated, the composition of the dissolved gas is found to be different from that of the original air on account of the solubility of oxygen in water being greater than that of nitrogen.

The question naturally suggests itself, whether the continual pouring into the atmosphere of so much carbon dioxide from all sources, the animal life on the globe as well as the product of so much decay and combustion, has not changed the composition of the air by reducing the percentage of oxygen. In reply to this it may be said that calculations based on the inhabitants at one thousand millions, and the amount of oxygen used in other ways at ten times that consumed by human beings, demonstrate that in eighteen hundred years the proportion of oxygen in the air would be decreased by only 0.1 per cent.

Analysis.—Moisture is determined by passing known quantities of air over calcium chloride and noting the increase in weight of the latter. Carbon dioxide is estimated in the same manner, using potassium hydrate instead of calcium chloride, or the air is passed into solution of barium hydrate and the resulting barium carbonate filtered off and weighed. Oxygen is estimated by taking a definite volume of pure dry air in a eudiometer tube

over mercury, adding a measured volume of pure hydrogen, and exploding the mixture by means of an electric spark. After cooling there will be a contraction equal to the volume of hydrogen and oxygen which have combined, the resulting volume of water being so small as to be disregarded.

Phosphorus has also been used for removing the oxygen. When this is carried out in a tube over mercury the resulting volume of nitrogen may easily be read off.

NITROGEN AND HYDROGEN.

AMMONIA.

Formula, NH_3. *Molecular Weight,* 16.93.

History.—Ammonium chloride, or sal ammoniac, appears to have been known from the earliest times, and the aqueous solution of the gas was described by the alchemists under the name of "spirits of hartshorn." Priestley, in 1774, was the first to prepare gaseous ammonia, by heating together sal ammoniac and lime, and collecting the gas over mercury. He gave to this gas the name of "alkaline air," which later became "volatile alkali."

Occurrence and Formation.—Ammonia, in combination with carbonic, nitric, and nitrous acids, exists in the air in minute quantities, being produced by the decomposition of organic matter. It is found in the Tuscan lagoons, probably combined with boron nitride, BN. It is also found as sulphate and chloride near active volcanoes, having been produced by the hot lava flowing over fertile soil containing nitrogen. Ammonia and its salts are formed in the dry distillation of many organic substances.

Formerly horns, hoofs, urine, and other animal products were distilled, and the ammonium carbonate thus produced neutralized with hydrochloric acid, the product after sublimation being known as sal ammoniac. At the present time our supply is obtained by a similar process, in which, however, coal is the material used. Bituminous coal yields on distillation about 2 per cent. of ammonia, which, therefore, occurs in the ammoniacal liquor formed during the manufacture of illuminating gas. In addition to free ammonia there are present in this ammoniacal gas-liquor the carbonate, sulphide, sulphate, and thiosulphate. The gas-liquor is usually distilled with lime, by which the ammonia is liberated and collected in a suitable receiver with some water. This distillate is neutralized with hydrochloric or sulphuric acid.

and the resulting ammonium chloride or sulphate purified and used for preparing the other ammonium salts.

Ammonia is also formed by the action of nascent hydrogen on nitrous or nitric acid. Finally, ammonia is produced in minute quantity by passing the electric spark through a mixture of nitrogen and hydrogen. It has been said that the elements do not unite directly, and this appears to be an insignificant exception to that statement. It is improbable that such combination should take place to any great extent, since ammonia gas is decomposed by the electric spark into its constituents.

Preparation.—Ammonia gas is prepared on a large scale by heating together in a glass or iron retort calcium hydrate and ammonium sulphate or chloride :

$$\underset{\text{Ammonium Sulphate.}}{(NH_4)_2SO_4} + \underset{\text{Calcium Hydrate.}}{Ca(OH)_2} = \underset{\text{Calcium Sulphate.}}{CaSO_4} + \underset{\text{Ammonia.}}{2NH_3} + \underset{\text{Water.}}{2H_2O}$$

For laboratory purposes it is usually preferable to heat the solution of ammonia which is supposed to contain ammonium hydrate :

$$NH_4OH = NH_3 + H_2O.$$

When required pure the gas must be passed over calcium oxide (quicklime) to remove moisture, and collected over mercury. As ordinarily needed it may be collected by "upward displacement;" that is, by holding an inverted vessel over the tube from which the gas is escaping, which gas, being lighter than air, rises and fills the vessel.

Properties.—Ammonia is a colorless gas, of a pungent, suffocating odor and a caustic taste. It has a density of 8.5, being a little more than half as heavy as air. The gas is liquefied by passing into a tube cooled to —40° by means of a mixture of ice and calcium chloride. It may also be liquefied by subjecting to a pressure of from six to seven atmospheres at ordinary temperatures. This liquid is colorless and highly refractive, and may be solidified by cooling to —75°. At —33.7° it boils, and in vaporizing absorbs large quantities of heat. On account of this property it is used in ice machines and in the several varieties of cooling apparatus used in breweries.

Ammonia is very soluble in water, one volume of the latter absorbing 1148 volumes of the gas at 0°, and about 600 volumes at ordinary temperatures. This solution, which is official in two strengths, will be described later.

Ammonia is not a combustible gas, although if it be mixed

with a small quantity of oxygen combustion readily takes place on the application of flame, with the formation of water, nitrogen and nitric acid. Ammonia is alkaline to litmus paper, and combines with acids, forming the well-known ammonium salts. The formula NH_4 represents a hypothetical compound which has many properties in common with those of sodium and potassium, and will be treated of in connection with them.

Uses.—Anhydrous liquid ammonia is prepared on a large scale for use in ice machines. It comes in commerce in large iron drums strong enough to withstand the pressure necessary to keep it in the liquid condition. The aqueous solution of ammonia is used largely in medicine and in the manufacture of pharmaceutical preparations.

Detection.—Ammonia and its solution are easily detected by the odor; in smaller quantities by bringing over the suspected solution a piece of moistened red litmus paper, which will be turned blue. Still more delicate is the reaction with fumes of hydrochloric acid. A rod moistened with the diluted acid is brought into some of the gas or over some of the warm solution, when immediately white fumes of ammonium chloride will form. When combined with acids, ammonia is detected by first liberating it from its combination with an alkali like potassium or sodium hydrate, and then applying one of the above tests for the gas, or the solution is acidified with hydrochloric acid and solution of platinic chloride added, when a yellow precipitate of ammonio-platinic chloride—$(NH_4)_2PtCl_6$—will slowly separate out in minute crystals. Einbrodt's reagent, consisting of a solution of mercuric chloride to which a minute quantity of an alkaline carbonate has been added, will detect the merest trace of ammonia or its compounds, if the latter are previously made alkaline, by forming a white precipitate or cloudiness. Nessler's reagent produces a brown precipitate with ammonium compounds, or if in very dilute solution a brown or yellow color. This reagent is made by adding to a solution of mercuric chloride a solution of potassium iodide until the precipitate at first formed is nearly all redissolved. Solution of potassium hydrate is then added to strongly alkaline reaction and the liquid allowed to settle until it becomes clear, when it is decanted from any sediment

Aqua Ammoniæ, U. S. P.—The solution of ammonia is official in two strengths, one, *aqua ammoniæ*, containing 10 per cent., by weight, of the gas, and the other, *aqua ammoniæ for-*

tior, containing 28 per cent., by weight, of the gas. That of 10 per cent. strength has the specific gravity 0.960 at 15°, and the stronger solution has the specific gravity 0.901 at 15°. The commercial "F. F. F." or "20°" water of ammonia contains about 14 per cent. of the gas.

The commercial solution of ammonia is sometimes prepared by the addition of milk of lime to gas liquor and passing the resulting gas into water, but it is difficult to purify such gas from empyreumatic products. This is accomplished in great part by passing the gas through a number of wash-bottles, and then through a series of tubes containing charcoal.

The solution is usually made, however, especially for medicinal purposes, by heating ammonium chloride or sulphate with milk of lime:

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2NH_3 + 2H_2O.$$

The gas is first passed through a little water to wash it, and then into a series of vessels filled with water, in which it is absorbed. The vessel nearest the generator becomes saturated first and is removed, the others are moved up to take its place, and a vessel of fresh water is attached at the end.

Properties.—Solution of ammonia is a colorless, transparent liquid with the pungent alkaline odor and taste of the gas. On the application of heat the solution evolves ammonia gas at a temperature considerably below the boiling point of water. The gas may also be removed by passing air into the solution. In this case there is a great absorption of heat by the escaping gas. With the stronger solution it is said that a temperature of —40° may be attained and a small quantity of mercury frozen.

Spiritus Ammoniæ, U. S. P.—This is an alcoholic solution of ammonia containing 10 per cent., by weight, of the gas. The gas is recommended to be prepared by heating the stronger aqueous solution, and the alcohol is directed to be recently distilled. It would probably be better to distil the alcohol from a little sodium hydrate, and then the darkening which it is intended to avoid would not occur. The specific gravity of the alcoholic solution is about 0.810 at 15.°

Impurities and Tests.—The same tests for purity apply to all the official solutions of ammonia. All should volatilize without residue. No empyreumatic odor should be developed on supersaturating some of the solution with sulphuric acid. All the

solutions should remain clear on mixing with five volumes of lime water, indicating the absence of carbonates. Hydrochloric acid when present may be detected by supersaturating with nitric acid and adding silver nitrate.

Sulphuric acid may be detected by similarly saturating with nitric acid and adding solution of barium chloride. Metallic impurities may be detected by the addition of hydrogen sulphide, and calcium salts by the addition of ammonium oxalate.

PRACTICAL EXERCISES.

(1) In a test-tube or evaporating dish mix equal quantities of powdered calcium oxide (quicklime) and ammonium chloride, with a few drops of water; the odor of ammonia will be immediately developed. In smaller quantities the gas may be recognized by holding over the mixture a strip of moistened red litmus paper, which will become blue.

(2) Prepare a larger quantity of the gas by heating in an ordinary flask some ammonia water; at comparatively low temperatures the gas is evolved freely. If it be desired to dry the gas it is accomplished by passing it over quicklime.

Ammonia is collected by *upward displacement;* that is, by passing the delivery-tube upward into a test-tube or jar inverted over it. The gas being lighter than air rises and displaces the latter.

(3) Place a vessel filled with ammonia gas, mouth downward, into some water and agitate slightly; the water will rise in the vessel rapidly, nearly filling it, showing the great solubility of the gas in water.

(4) On applying a lighted taper to the gas the latter does not burn; if, however, it be mixed with oxygen it will ignite readily. A lighted taper is extinguished when plunged into the gas.

DIAMINE, $N_2H_4 = H_2N.NH_2$.

HYDRAZINE.

This compound was discovered in 1887, and is obtained when certain nitrogenous organic compounds are decomposed. In many respects it resembles ammonia, being a colorless gas, with a peculiar ammoniacal odor and a strong alkaline reaction. It is very soluble in water, forming a hydrate of the formula $N_2H_4.H_2O$. This combines with acids like ammonia, but with twice the combining power, the formula of the sulphate being $N_2H_4H_2SO_4$, and the chloride $N_2H_4(HCl)_2$.

HYDROXYLAMINE, NH_2OH

This compound is prepared by the action of nascent hydrogen on some oxygen compound of nitrogen, for example, nitric acid:

$$HNO_3 + 3H_2 = NH_2OH + 2H_2O.$$

Like ammonia and hydrazine, it is soluble in water. This solution, which is the only form in which it is known, is a colorless, odorless, alkaline, and strongly reducing liquid, which precipitates the metals gold, mercury, and silver from solutions of their salts.

On the application of heat to the solution partial decomposition takes place, ammonia, hydroxylamine, and water distilling.

Hydroxylamine unites with acids, the chloride having the formula $NH_2OH.HCl$, or NH_4OCl.

NITROGEN AND CHLORINE.

NITROGEN CHLORIDE, NCl_3.

Preparation.—It is prepared by acting on ammonium chloride with chlorine:

$$NH_4Cl + 3Cl_2 = NCl_3 + 4HCl.$$

It is also formed when solution of ammonium chloride is submitted to the electric current; the chlorine which forms at the positive pole acts on the ammonium chloride. In order to obtain the pure product, the oil which separates in one of the above methods is well washed with cold water to remove ammonium chloride and then dried in a current of chlorine.

Properties.—Nitrogen chloride is a yellow oil of the specific gravity 1.653. It possesses a disagreeable, pungent odor, and the vapor which always escapes on exposure to air attacks the eyes. It is one of the most violent explosives known. The explosion takes place on the slightest provocation, as exposure to sunlight or contact with many kinds of organic matter, as caoutchouc or turpentine.

NITROGEN IODIDE, NHI_2.

Preparation.—It is prepared by powdering a little iodine in a mortar and covering with solution of ammonia; after standing ten minutes the insoluble portion is collected on a filter.

Properties.—While moist, nitrogen iodide is comparatively safe in small quantities, but so soon as it becomes dry it explodes on the slightest touch. It is a black powder, and is variously stated by different authors to have the composition NI_3 or NHI_2. It is probable that the substance obtained as above described is a mixture of two or more compounds.

NITROGEN FLUORIDE, NF_3.

This is prepared, like nitrogen chloride, by the electrolysis of ammonium fluoride. It is a highly explosive compound.

NITROGEN AND OXYGEN.

Nitrogen combines with oxygen in five different proportions, three of which form acids, as follows:

Oxides.	Acids.
Nitrogen monoxide, N_2O.	Hyponitrous acid, HNO.
Nitrogen dioxide, N_2O_2.	
Nitrogen trioxide, N_2O_3.	Nitrous acid, HNO_2.
Nitrogen tetroxide, N_2O_4.	
Nitrogen pentoxide, N_2O_5.	Nitric acid, HNO_3.

NITROGEN MONOXIDE.

Formula, N_2O. *Molecular Weight*, 43.74.

History.—Nitrogen monoxide, which is also known by the names nitrous oxide and laughing gas, was discovered by Priestley in 1772.

Preparation.—This gas is formed when zinc is dissolved in diluted nitric acid:

$$\underset{\text{Zinc.}}{4Zn} + \underset{\substack{\text{Nitric}\\\text{Acid.}}}{10HNO_3} = \underset{\substack{\text{Zinc}\\\text{Nitrate.}}}{4Zn(NO_3)_2} + \underset{\substack{\text{Nitrogen}\\\text{Monoxide.}}}{N_2O} + \underset{\text{Water.}}{5H_2O.}$$

The usual method of preparing the gas is by heating ammonium nitrate to 200°, when it is decomposed into water and nitrogen monoxide.

$$\underset{\substack{\text{Ammonium}\\\text{Nitrate.}}}{NH_4NO_3} = \underset{\substack{\text{Nitrogen}\\\text{Monoxide.}}}{N_2O} + \underset{\text{Water.}}{2H_2O.}$$

The most probable impurity in ammonium nitrate is ammonium chloride, which would occasion the presence of chlorine in the gas. It is, therefore, best to pass the gas through three wash-bottles, one of ferrous sulphate solution to remove the other oxides of nitrogen, one of sodium hydrate solution to remove chlorine, and, finally, one of pure water. Since one volume of water absorbs three-fourths of a volume of nitrogen monoxide, a larger yield is obtained by warming the water over which it is collected. On the large scale it is customary to use iron retorts, and after passing the gas through the washings above mentioned to run it into large gasometers over water, taking care to keep the same water in constant use, as after the latter is once saturated there is comparatively little loss.

Properties.—Nitrogen monoxide is a colorless gas of a faint, peculiar odor and a sweetish taste. It is twenty-two times heavier than hydrogen. Under ordinary atmospheric pressure it liquefies at —88°, and at —100° becomes solid. It may also be liquefied at 0° by a pressure of thirty atmospheres. Liquid nitrogen monoxide is colorless and very mobile, and has a specific gravity of 0.9369 at 0°. A drop of the liquid, when brought in contact with the skin, will cause a blister, and water poured on the liquid is immediately frozen, producing at the same time an explosive evolution of the gas. Carbon disulphide dissolves the liquid, and on bringing the mixture under the receiver of an air-pump and exhausting, the temperature of the solution may be reduced to —140°.

Gaseous nitrogen monoxide supports the combustion of many substances almost as actively as oxygen.

Uses.—The gas is extensively used by inhalation in minor surgery and dentistry, where a short anæsthetic effect is desired. For this purpose the gas must be perfectly pure. One of the greatest safeguards is to have pure ammonium nitrate from which to make it. When mixed with air or oxygen the gas produces a condition of partial insensibility, in which the patient often becomes hysterical, laughing immoderately, hence the name *laughing gas.*

It is manufactured on a large scale, and pumped into strong steel cylinders under a pressure of sixty-five atmospheres, and at a temperature of 5° to 10°. There are two sizes of these cylinders, one containing one hundred gallons, and the other four hundred and fifty to five hundred gallons of the gas. The contents of the small cylinders weigh about one and a half pounds, that of the large cylinders about seven pounds. The gas is drawn into rubber bags before administering, as a low temperature is caused by its release from pressure. A solution of the gas, under the name of "nitrous oxide water," is made by forcing it into water under a pressure of five atmospheres. This solution is reputed to have some medicinal value.

PRACTICAL EXERCISES.

(1) Heat a small quantity of ammonium nitrate in a test-tube, to which is attached a delivery-tube, as in the preparation of oxygen. The gas is nitrogen monoxide and may be collected over water.

(2) Plunge a lighted taper into the gas; it is not combustible, but it increases the energy of the combustion of the taper; it is, therefore, not a combustible gas, but it supports combustion with an energy almost equal in many cases to that of oxygen.

HYPONITROUS ACID.

Formula, HNO. *Molecular Weight,* 30.97.

This acid is known only in dilute solution or in combination with certain bases. When an aqueous solution of potassium nitrate is treated with sodium amalgam in the proportion of four atoms of sodium to one molecule of the nitrate, potassium hyponitrite is formed:

$$KNO_3 + 2H_2 = KNO + 2H_2O.$$

On carefully neutralizing with acetic acid, and adding silver nitrate, a yellow precipitate of silver hyponitrite, AgNO, separates. From researches on a volatile compound of hyponitrous acid, it is probable that its formula is $H_2N_2O_2$, or double that above given. This is rendered more evident by the fact that some of the acid salts have been prepared,

which would require the presence of two hydrogen atoms in the molecule. All the salts are quite unstable.

NITRIC OXIDE, OR NITROGEN DIOXIDE.

Formula, NO, *or* N_2O_2. *Molecular Weight*, 59.62.

Preparation.—When nitric acid is added to copper turnings, in a suitable vessel, nitrogen dioxide is evolved:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + N_2O_2 + 4H_2O.$$

Mercury, silver, and some other metals will also give this result. As it comes off at first the gas is of a reddish color, but when the air is all driven out the compound becomes colorless and may then be collected over water. As prepared in this manner the gas is not quite pure, but it may be purified by passing it into a cold, concentrated solution of ferrous sulphate, which absorbs it, and afterward, when heated, gives it off pure. Nitrogen dioxide may more readily be obtained pure by acting on ferrous sulphate with potassium nitrate and sulphuric acid:

$$6FeSO_4 + 2KNO_3 + 5H_2SO_4 = 3Fe_2(SO_4)_3 + 2KHSO_4 + 4H_2O + N_2O_2.$$

Ferrous Sulphate.	Potassium Nitrate.	Sulphuric Acid.	Ferric Sulphate.	Acid Potassium Sulphate.	Water.	Nitrogen Dioxide.

The proportions for the above reaction are 30 grammes of potassium nitrate, 240 grammes of ferrous sulphate, and 250 c.c. of a mixture of one volume concentrated sulphuric acid and three volumes of water.

Properties.—Its critical temperature is —93.5° C. and critical pressure 71.2 atmospheres. It combines with the oxygen of the air, forming red fumes of the tetroxide. It is not a combustible gas, nor does it support ordinary combustion. Phosphorus when melted will not ignite in it, but if previously ignited it will burn with great brilliancy. A mixture of nitrogen dioxide and carbon disulphide, when ignited, burns with a blinding, bluish-white flame, which is remarkable for its chemically active rays.

NITROGEN TRIOXIDE.

Formula, N_2O_3. *Molecular Weight*, 75.50.

Preparation.—When nitric acid of specific gravity 1.35 is heated with starch, orange-red fumes are evolved, which consist of a mixture of nitrogen trioxide and tetroxide. On passing these vapors, mixed with nitric oxide, N_2O_2, through a hot tube and then into a vessel surrounded by a freezing mixture, the pure

trioxide will be obtained. The mixed vapors, when cooled, form a green liquid; but pure trioxide, at —10°, is an indigo-blue liquid. It does not solidify at —82°, and at 0° the liquid begins to decompose into N_2O_2 and N_2O_4. With a small quantity of water nitrogen trioxide forms nitrous acid:

$$N_2O_3 + H_2O = 2HNO_2.$$

With a large quantity of water decomposition takes place and nitric acid results.

NITROUS ACID.

Formula, HNO_2. *Molecular Weight,* 46.69.

Preparation.—This acid is prepared by adding liquefied nitrogen trioxide to ice water. It is so unstable that it cannot be obtained in a state of purity. It is a blue liquid, which is readily decomposed into nitric acid and nitric oxide.

Nitrites.—The salts of nitrous acid are quite stable compounds, and are usually prepared by carefully heating the nitrates. On account of their solubility in alcohol this substance is used to separate the nitrite from the undecomposed nitrate. The addition of copper or lead is often resorted to in order to facilitate the reduction by combining with the liberated oxygen.

The nitrites are distinguished from the nitrates by giving off reddish fumes on the addition of acids. All the nitrites are soluble in water, and most of them are soluble in alcohol.

NITROGEN TETROXIDE, OR PEROXIDE.

Formula, N_2O_4, *or* NO_2. *Molecular Weight,* 91.48. - 91.35

Preparation.—This compound is prepared by bringing together two volumes of nitric oxide, NO, and one volume of oxygen. The resulting red gas may be condensed to a liquid, or even to a solid, by passing it into a tube immersed in a freeezing mixture.

Many nitrates on heating give off this gas. Lead nitrate is usually employed:

$$\underset{\text{Lead Nitrate.}}{2Pb(NO_3)_2} = \underset{\text{Lead Oxide.}}{2PbO} + \underset{\text{Nitrogen Tetroxide.}}{2N_2O_4} + \underset{\text{Oxygen.}}{O_2}.$$

The vapors of the tetroxide are separated from the oxygen by passing the two through a freezing mixture, whereby the former is condensed.

When arsenous oxide, As_2O_3, is gently heated in a retort with nitric acid of the specific gravity 1.393, the tetroxide is given off abundantly, and condensed as described above:

$$\underset{\text{Arsenous Oxide.}}{As_2O_3} + \underset{\text{Nitric Acid.}}{4HNO_3} = \underset{\text{Arsenic Oxide.}}{As_2O_5} + \underset{\text{Nitrogen Tetroxide.}}{2N_2O_4} + \underset{\text{Water.}}{2H_2O}.$$

The small amount of nitrogen trioxide, N_2O_3, which is produced at the same time, may be converted into the tetroxide by passing a slow stream of oxygen into the condensed vapors.

Properties.—Nitrogen tetroxide is a liquid which shows some remarkable changes of color: at —20° it solidifies to a mass of colorless crystals, when liquefied at a little above this temperature it is still free from color, but commences to darken, and when the temperature reaches 0° it is yellow. Above this it gradually shades into a brown, until at 26° it boils, giving off deep, reddish-brown fumes. At a little above the boiling point it has a vapor density nearly represented by the formula N_2O_4, but as the temperature increases the vapor become darker in color, and at 140° the density corresponds to the formula NO_2.

The liquid is very corrosive and a powerful oxidizer, and the fumes are very irritating. With water nitrogen tetroxide decomposes into nitric acid and nitric oxide.

NITROGEN PENTOXIDE.

Formula, N_2O_5. *Molecular Weight*, 107.26.

Preparation.—When dry chlorine is passed over dry silver nitrate in a U tube heated to 95°, there is first formed nitroxyl chloride, NO_2Cl, which by further action on the silver nitrate at 60° gives nitrogen pentoxide:

$$AgNO_3 + Cl_2 = NO_2Cl + AgCl + O,$$
$$AgNO_3 + NO_2Cl = N_2O_5 + AgCl.$$

It is also prepared by adding phosphorus pentoxide to anhydrous nitric acid cooled to 0°, and carefully distilling the mixture in a retort attached to a well-cooled receiver:

$$2HNO_3 + P_2O_5 = N_2O_5 + 2HPO_3.$$

The products are nitrogen pentoxide and metaphosphoric acid.

Properties.—Nitrogen pentoxide is a white, colorless, crystalline solid. The crystals melt at 29.5° to a dark-yellow liquid, which boils with decomposition at 45° into nitrogen tetroxide and oxygen.

When heat is applied suddenly this decomposition takes place with explosive violence. It dissolves in water with evolution of heat and forms nitric acid:

$$N_2O_5 + H_2O = 2HNO_3.$$

When brought in contact with many substances, as phosphorus and sulphur, it oxidizes them, the former with ignition; organic matter is also violently attacked.

Nitrogen pentoxide combines with nitric acid to form pernitric acid, having the formula $N_2O_5.2HNO_3$. This is a liquid at ordinary temperatures, having the specific gravity 1.642 at 18°, but is crystalline at 5°. It corresponds to disulphuric acid.

NITRIC ACID.

Formula, HNO_3. *Molecular Weight*, 62.57.

History.—Nitric acid was prepared by Geber, in the eighth century, by the distillation of saltpetre with alum or copper sulphate. The composition of the acid was first made known through the investigations of Lavoisier, in 1776, and Cavendish, in 1784.

Occurrence and Formation.—Nitric acid is not found in the free state in nature, but in combination with potassium, sodium, calcium, magnesium, and ammonium it is widely distributed. In warm countries these salts occur as an efflorescence on the surface of the ground and walls where organic matter is decaying. The largest known deposits are the nitrate of soda beds in the provinces of Tarapaca and Atacama, rainless districts on the Peruvian coast. The origin of these great deposits is a matter of conjecture, but it has been suggested that they are the result of the decomposition of sea plants and animals deposited by the receding ocean.

The production of potassium nitrate is carried out artificially in the nitre plantations of India. This was formerly the chief source of the world's supply of potassium salt or saltpetre. Animal matter is mixed with lime and ashes, and the mass exposed to the air but sheltered from the rain. The pile is kept moistened with urine for three years, when it is lixiviated with water. A cubic meter is said to yield twenty kilos. of nitre.

Nitric acid is formed when hydrogen is burned in oxygen containing a small quantity of nitrogen.

When air in a glass globe is submitted to a series of electric sparks, red fumes of nitrogen tetroxide are formed, which in the presence of water are decomposed with the formation of nitric acid. When the air is compressed the production of red fumes is increased.

Preparation.—On the small scale nitric acid is prepared by

heating in a glass retort equal parts of potassium nitrate and sulphuric acid :

$$\underset{\text{Potassium Nitrate.}}{KNO_3} + \underset{\text{Sulphuric Acid.}}{H_2SO_4} = \underset{\text{Acid Potassium Sulphate.}}{KHSO_4} + \underset{\text{Nitric Acid.}}{HNO_3}.$$

The apparatus becomes filled with reddish-brown vapors, and the liquid which condenses has a yellowish color on account of the presence of nitrogen tetroxide. The absolute acid is prepared by placing the above distillate with 2 volumes of concentrated sulphuric acid in a retort connected with a well-cooled receiver, and applying a gentle heat. The distillate in this case is freed from color by warming gently and passing through it a current of air to remove the fumes of the lower oxides of nitrogen. The acid can in this way be made to contain about 99.5 per cent. of HNO_3.

On the large scale, 700 parts of sodium nitrate or Chili saltpetre are heated in a cast-iron retort with 600 parts of sulphuric acid of the specific gravity 1.84, and the retort connected with 25 receivers, which contain such a quantity of water as will make the acid of the specific gravity 1.35 to 1.42. The product in this case contains chlorine and iodic acid, and is purified by distilling from glass retorts. The chlorine passes over first, then the receivers are changed, when the pure acid comes over until only a small residue is left in the retort ; this residue contains iodic acid, sulphuric acid, and sodium sulphate. Half the quantity of sulphuric acid may be used in the above processes, when neutral sodium sulphate will remain in the retort :

$$\underset{\text{Sodium Nitrate.}}{2NaNO_3} + \underset{\text{Sulphuric Acid.}}{H_2SO_4} = \underset{\text{Sodium Sulphate.}}{Na_2SO_4} + \underset{\text{Nitric Acid.}}{2HNO_3}.$$

While this is more economical of original material, the higher heat necessary causes a greater decomposition of nitric acid and a more destructive action on the retort. The resulting sodium or potassium sulphate is more difficult to remove, as it remains as a hard, solid mass, while the acid sulphate is in a liquid condition at a moderate temperature and may be poured out.

Properties.—Nitric acid is a colorless, fuming, very corrosive liquid. When absolute, it has a specific gravity of 1.530, and commences to boil at 86°, but on account of partial decomposition into water, nitrogen tetroxide, and oxygen, the temperature rises, until at 120.5° a liquid containing 68 per cent. of the acid distils over unchanged, and has a specific gravity of 1.414

at 15°. When a weaker acid is heated, water is first given off until the acid attains the strength of the above, when it distils unchanged. This is the *Acidum Nitricum*, U.S.P. Commercial nitric acid has approximately a specific gravity of 1.42, and contains 69.4 per cent. of absolute nitric acid.

Nitric acid is a powerful oxidizing agent. It first oxidizes most of the metals and then dissolves them, forming nitrates. Sulphur, phosphorus, and carbon are oxidized by it to oxides or acids. Many organic bodies, like turpentine, are inflamed at once on coming in contact with it, while other organic compounds are merely turned yellow. A number of substances, like cotton and benzene, undergo a process of *nitration* when brought in contact with the concentrated acid. In this operation the group NO_2 replaces hydrogen in the compound. With cotton or cellulose, gun cotton (cellulose nitrate) is formed, with glycerin, nitroglycerin (glyceryl nitrate), and with benzene, nitrobenzene.

The red *fuming* nitric acid differs from the ordinary variety by containing the oxides of nitrogen in solution. It is usually prepared by the method mentioned above, in which a quantity of sulphuric acid is used sufficient to decompose the nitre with formation of neutral sodium sulphate. The high heat necessary to carry out this process decomposes a part of the nitric acid with the formation of red fumes.

Detection.—Nitric acid is easily detected by its action on copper, which it dissolves with a blue color, giving off abundant brown-red fumes at the same time. When wool and silk are brought in contact with strong nitric acid they are colored yellow, and the color is not discharged by ammonia. The acid destroys the blue color of indigo solution, forms a dark ring when brought in contact with a crystal of ferrous sulphate and sulphuric acid, is colored red by brucine, and gives off ammonia when made strongly alkaline with potassium hydrate and heated with zinc.

Impurities and Tests.—Mineral impurities are detected by evaporating to dryness, when no residue should remain. The absence of hydrochloric acid is determined by silver nitrate, and the freedom from sulphuric acid by barium chloride. On diluting with water and adding a small quantity of solution of starch, no blue color should be produced, thus showing the absence of iodine. Iodic acid may be detected with this test by first adding some hydrogen sulphide.

Nitrates.—Nitric acid is monobasic and forms with bases, by replacement of its one hydrogen atom, a series of salts known as

nitrates. The most of them are prepared by dissolving the metal in the acid. In the case of the alkalies and alkaline earths, the carbonate, oxide, or hydrate is used to neutralize the acid.

The nitrates are nearly all soluble in water, the exceptions being a few of the basic salts which this acid forms. On the application of heat they evolve, first oxygen and then nitrogen tetroxide, or a mixture of nitrogen and oxygen, leaving an oxide of the metal.

PRACTICAL EXERCISES.

Place a small quantity of potassium nitrate in a test-tube, add sulphuric acid, and apply a gentle heat; brown, strongly acid fumes will be given off. Dilute with water and add indigo solution; the latter loses its blue color, becoming yellow or brown. This is a characteristic test for nitric acid.

Acidum Nitrohydrochloricum, U. S. P.—This substance, which is also known by the names aqua regia and nitromuriatic acid, was first prepared by Geber, who dissolved ammonium chloride in nitric acid. Basil Valentine appears to have given it the name *aqua regia*, and suggested the method for preparing it, used at the present time, by mixing nitric and hydrochloric acids.

Preparation.—The U. S. P. recommends the preparation of it by mixing 18 parts of nitric with 82 parts of hydrochloric acid, all by volume. They should be mixed in an open vessel, allowed to stand until effervescence has ceased, and preserved in partly filled bottles in a cool place. The compounds formed by the combination of the two acids are chlorine and nitrosyl chloride:

$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O.$$

Properties.—Nitrohydrochloric acid is a "golden-yellow, fuming, very corrosive liquid, having a strong odor of chlorine" and a strongly acid reaction. It is wholly volatilized on the application of heat, and readily dissolves gold and platinum. This solvent action depends largely on the chlorine which is present.

PHOSPHORUS.

Symbol, P. *Atomic Weight,* 30.75. *Valence,* III.

History.—Phosphorus was discovered by the alchemist Brandt, in 1669, at Hamburg. He prepared it by distilling a mixture of evaporated urine and sand. A hundred years later it was shown by Gahn to be a constituent of bones, and in 1771 Scheele published a method for preparing it from this source.

Occurrence.—Phosphorus is never found native in the free state, but chiefly as calcium phosphate, the principal constituent of bones, as well as of the minerals *apatite* and *phosphorite*. Very extensive deposits of calcium phosphate are found near Charleston, South Carolina, in Florida, and in several other of the Southern States. This "phosphate rock," as it is called, contains also some iron, alumina, carbonic acid, and fluorine. It is collected and shipped in enormous quantities to many parts of the world to be used for fertilizing purposes.

Phosphorus is, further, very widely distributed in comparatively small quantities. It is always found in plant and animal tissues, in the soil, and in sea water. The source of the element is largely bones, although a portion of that made in England is prepared from *sombrerite*, a mineral from the island of Sombrero in the West Indies, consisting of impure calcium phosphate.

Preparation.—The bones are freed from fat by carbon disulphide or petroleum benzin, and from gelatin by superheated steam. They are then burned to whiteness. The resulting white boneash is composed of 86 per cent. calcium phosphate, $Ca_3(PO_4)_2$, and small quantities of magnesium phosphate and calcium carbonate and fluoride.

This boneash or its equivalent, the calcined spent boneblack from the sugar refiners, or *sombrerite*, is treated with an equal weight of 50 per cent. sulphuric acid:

$$\underset{\text{Calcium Phosphate.}}{Ca_3(PO_4)_2} + \underset{\text{Sulphuric Acid.}}{2H_2SO_4} = \underset{\text{Acid Calcium Phosphate.}}{CaH_4(PO_4)_2} + \underset{\text{Calcium Sulphate.}}{2CaSO_4}.$$

The solution of acid phosphate is decanted from the calcium sulphate, evaporated to dryness, and heated to redness, by which it loses water and is converted into calcium metaphosphate:

$$\underset{\text{Acid Calcium Phosphate.}}{CaH_4(PO_4)_2} = \underset{\text{Calcium Metaphosphate.}}{Ca(PO_3)_2} + \underset{\text{Water.}}{2H_2O}.$$

The calcium metaphosphate is very intimately mixed with charcoal, and gradually heated in earthenware retorts to a white heat, when the following reaction takes place:

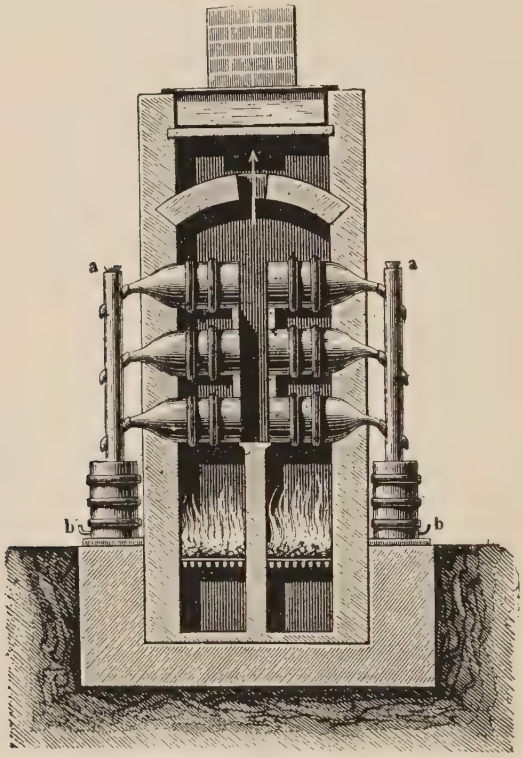
$$\underset{\text{Calcium Metaphosphate.}}{3Ca(PO_3)_2} + \underset{\text{Charcoal.}}{10C} = \underset{\text{Phosphorus.}}{P_4} + \underset{\text{Calcium Phosphate.}}{Ca_3(PO_4)_2} + \underset{\text{Carbon Monoxide.}}{10CO}.$$

The yield amounts to two-thirds of the phosphorus which is present. The whole of the phosphorus may be recovered by adding enough sand to convert the calcium into silicate, according to the following reaction:

$$\underset{\text{Calcium Metaphosphate.}}{2Ca(PO_3)_2} + \underset{\text{Silica.}}{2SiO_2} + \underset{\text{Charcoal.}}{10C} = \underset{\text{Phosphorus.}}{P_4} + \underset{\text{Calcium Silicate.}}{2CaSiO_3} + \underset{\text{Carbon Monoxide.}}{10CO}.$$

The furnace and retorts used in the above distillation are shown in Fig. 110. The yield is from 8 to 10 per cent.. of the

FIG. 110.



Preparation of phosphorus.

bones used. Phosphorus at this stage still contains impurities carried over mechanically in the process of distillation, and from these it must be further purified. This is accomplished by redistilling from iron retorts, by pressing through chamois leather under water, or by treating the melted phosphorus under water with a mixture of sulphuric acid and potassium dichromate, three and a half parts of each of these compounds being used for every one hundred parts of the element.

After the purification process the molten phosphorus is run into glass or copper to solidify in the form of sticks, and, after

cutting under water, is preserved under the same liquid in barrels, or, better, in sealed tin cans.

Most of the world's supply of this element comes from two manufactories, one at Oldbury, England, and one at Lyons, France. Smaller quantities are produced in Russia, Sweden, and the United States. The present output amounts to about two thousand five hundred tons annually.

For the thermo-electric process of preparation, see p. 872.

Properties.—Like many of the other elements, phosphorus exists in several allotropic forms. That obtained by the above methods is known as *ordinary* or *octohedral* phosphorus.

This variety is a colorless, transparent to translucent, wax-like solid. At ordinary temperatures it is sufficiently soft to be cut by a knife, but at lower temperatures it becomes more brittle. It has a specific gravity of 1.83 at 10°, and at 44° it melts to a colorless liquid. It boils at 290°, air, of course, being excluded. Between the temperatures of 500° and 1000° the vapor of phosphorus has a density of 61.92, indicating a formula for the molecule of P_4. At a higher temperature it is less, indicating that the molecule under these conditions is made up of a less number of atoms.

Phosphorus is insoluble in water, soluble in 350 parts of absolute alcohol at 15°, and in 240 parts of boiling absolute alcohol, in 80 parts of absolute ether, and in about 50 parts of any fatty oil. Chloroform and benzene dissolve it in considerable quantity, and carbon disulphide is probably its best solvent, dissolving from 18 to 20 times its weight without losing its fluidity. All solutions of phosphorus in carbon disulphide should be preserved with the greatest care. When spilled or otherwise exposed the solvent rapidly evaporates, leaving the phosphorus in such a finely divided condition that it inflames spontaneously. Phosphorus may be powdered by melting under water and agitating until cold; many saline solutions facilitate this division. When exposed to a damp air at ordinary temperatures, phosphorus undergoes slow oxidation, giving off garlic-smelling fumes of phosphorus and phosphoric acids, which are luminous in the dark. It is a very inflammable element, igniting in the air spontaneously at 50°. For this reason it is kept and cut under water. The sticks of phosphorus which are kept under water, exposed to the light, become covered with a white, opaque film, which slowly turns red and peels off. This is due to slight oxidation, and may be prevented by excluding light, and using for covering a pure water that has

been recently boiled to remove oxygen and cooled. In pure oxygen phosphorus is not luminous below 15°, but becomes so immediately on the introduction of an inert gas like nitrogen, or by rarefying the oxygen.

Phosphorus combines directly with many elements, like sulphur, chlorine, bromine, iodine, and, at higher temperatures, with many of the metals. With hydrogen and nitrogen it does not combine directly. On account of its affinity for oxygen, it reduces many metallic salts when placed in their aqueous solutions, precipitating the metal. Nitric acid oxidizes phosphorus to phosphoric acid, and solutions of the alkaline hydrates convert it, on boiling, into hypophosphite of the base with evolution of hydrogen phosphide.

Red or *amorphous* phosphorus is an allotropic modification discovered by Schrötter in 1845. It is prepared by heating the ordinary variety in a nearly closed iron vessel to 240° or 250°, or more quickly by having the vessel closed tightly and heating to 300° under pressure, when the conversion takes place in a few moments. It is necessary to introduce an inert gas like nitrogen before heating the phosphorus. At 260°, in an open vessel, the amorphous variety is reconverted into ordinary phosphorus, with evolution of considerable heat. Amorphous phosphorus, prepared as above described, contains some of the ordinary variety, from which it is freed by treatment with carbon disulphide, which leaves the red variety in a state of purity. When purified, amorphous phosphorus has a specific gravity of 2.15. It is not affected by solvents and does not inflame in air until the temperature reaches 260°. A slow oxidation to phosphoric acid takes place at ordinary temperatures.

Amorphous phosphorus is said not to be poisonous, while the ordinary variety is very energetic in its action on the human system. The poisonous results obtained from the former are probably due to the presence of the latter as an impurity.

A third variety, known as *rhombohedral* or *metallic* phosphorus, is obtained by heating the ordinary variety in sealed tubes with metallic lead for ten hours, at a little below a red heat. After cooling, the lead is dissolved in diluted nitric acid, which leaves a mass of dark-red crystals. This modification has a specific gravity of 2.34 at 15°, and requires a temperature of 358° to convert it into the ordinary form. This variety is also obtained when the amorphous phosphorus is heated in a sealed tube to 580°.

Uses.—Phosphorus is used in medicine and in the manufacture of many chemical compounds, frequently without being a constituent of the product, for example, in the preparation of methyl and ethyl iodides. Its most extensive use, however, is in the manufacture of matches and as a poison for vermin.

In the manufacture of matches, phosphorus is submerged in a warm concentrated solution of glue, and then rapidly stirred to prevent it reaching the surface in a mass and igniting. When it has become uniformly mixed, the other ingredients are added, and the matches, previously tipped with paraffin, are dipped. Many mixtures have been proposed; the following is characteristic: phosphorus, 2 parts; manganese dioxide, 1 part; chalk, 3 parts; lampblack, ⅛ part, and glue, 5 parts. In many of the mixtures potassium chlorate or nitrate is used.

On account of the danger to workmen engaged in the manufacture of matches, not only from the ignition of the phosphorus, but also because of the poisonous character of the fumes, it has been proposed to use amorphous phosphorus in the process In this country, however, the suggestion has not met with much favor. In Europe the so-called *safety matches* are extensively manufactured and used. In order to ignite them these matches require to be rubbed on a certain material. The matches are tipped with a mixture of potassium chlorate, 32 parts; potassium dichromate, 12 parts; red oxide of lead, 32 parts, and antimony sulphide, 24 parts. The composition on the box is made up of amorphous phosphorus and antimony sulphide. These matches may sometimes be ignited by quickly drawing them over a piece of ground glass or a sheet of smooth white paper.

Impurities.—Phosphorus frequently contains arsenic derived from the sulphuric acid used in its manufacture, and at the same time it may be contaminated with sulphur.

The following U. S. P. test is sufficient to identify these impurities: "Add 3 gm. of Phosphorus to 15 c.c. of nitric acid diluted with 15 c.c. of distilled water in a flask having the capacity of 50 c.c., and digest the mixture at a gentle heat on a water-bath, until the Phosphorus is dissolved. Transfer the solution to a capsule, and evaporate it until no more nitrous vapors are given off, and then dilute the solution to 30 c.c. with distilled water. Heat 20 c.c. of the diluted solution to about 70° for half an hour, passing hydrogen sulphide through it during the half-hour's heating, and then until the liquid has become cold. If the liquid be now allowed to stand at rest during twenty-four hours, not more

than a very small quantity of lemon-yellow precipitate should be visible (limit of *arsenic*).

"On adding barium chloride T.S. to the remainder of the liquid, not more than a slight opalescence should be produced (limit of *sulphur*)."

PHOSPHORUS AND HYDROGEN.

Phosphorus combines with hydrogen in three proportions:

PH_3, gaseous hydrogen phosphide,
P_2H_4, liquid hydrogen phosphide,
P_4H_2, solid hydrogen phosphide.

Gaseous hydrogen phosphide is prepared by heating hypophosphorous acid:

$$\underset{\text{Hypophosphorous Acid.}}{2H_3PO_2} = \underset{\text{Phosphoric Acid.}}{H_3PO_4} + \underset{\text{Hydrogen Phosphide.}}{PH_3},$$

and by heating phosphorous acid:

$$\underset{\text{Phosphorous Acid.}}{4H_3PO_3} = \underset{\text{Phosphoric Acid.}}{3H_3PO_4} + \underset{\text{Hydrogen Phosphide.}}{PH_3}.$$

Hydrogen phosphide is also evolved when phosphorus is heated with a solution of potassium hydrate:

$$\underset{\text{Potassium Hydrate.}}{3KOH} + \underset{\text{Phosphorus.}}{P_4} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Potassium Hypophosphite.}}{3KH_2PO_2} + \underset{\text{Hydrogen Phosphide.}}{PH_3}.$$

The last is the usual method of preparing the gas, and it is important to observe certain precautions. The air must first be displaced by a stream of carbon dioxide or illuminating gas. The delivery-tube is then put under the surface of water and heat applied. Some time after boiling commences, the escaping gas, as it comes in contact with air, inflames spontaneously with a slight report, and forms a beautiful ring of white smoke.

In order to obtain the gas perfectly pure, it is passed through a tube immersed in a freezing mixture, by which means the liquid hydrogen phosphide is condensed. When prepared from phosphonium iodide none of the liquid compound is formed.

Properties.—Hydrogen phosphide, when pure, is a colorless gas with a disagreeable fishy odor. It inflames when heated to 100°, or by slight concussion, forming metaphosphoric acid.

Hydrogen phosphide is a compound analogous to ammonia, and combines with hydrochloric, hydrobromic, and hydriodic acids, forming phosphonium chloride, PH_4Cl, phosphonium bromide, PH_4Br, and phosphonium iodide, PH_4I.

Liquid hydrogen phosphide, P_2H_4, is formed by passing the gas obtained from phosphorus and potassium hydrate through a freezing mixture, by which the liquid phosphide is condensed. It is also formed by the action of water on calcium phosphide:

$$\underset{\text{Dicalcium Diphosphide.}}{Ca_2P_2} + \underset{\text{Water.}}{4H_2O} = \underset{\text{Calcium Hydrate.}}{2Ca(OH)_2} + \underset{\text{Hydrogen Phosphide.}}{P_2H_4}.$$

Properties.—This is a colorless, strongly refracting liquid, which inflames spontaneously in contact with air. On exposure to light without access of air it readily decomposes into gaseous and solid hydrogen phosphide. This substance is analogous to the ammonium compound, *hydrazine*, N_2H_4, but is not so stable.

Solid hydrogen phosphide, P_4H_2, is formed when calcium phosphide is dissolved in warm concentrated hydrochloric acid, with exclusion of air. It is a yellow, odorless, and tasteless powder, which on exposure to air changes to an orange color. When heated to 70° with exclusion of air it is decomposed into phosphorus and hydrogen.

PHOSPHORUS AND THE HALOGENS.

Phosphorus combines with the halogens at ordinary temperatures, in some cases with evolution of heat and light. It forms at least two compounds with each, acting with an equivalence of three or five, according to the amount of the halogen present at the time of combination.

Phosphorus trichloride, PCl_3, is prepared by passing dry chlorine into a retort in which there is amorphous phosphorus; a moderate heat is applied to the retort, and the resulting vapors of the chloride are conducted into a well-cooled receiver. When the phosphorus is kept in excess the product is nearly pure, but if the chlorine be slightly in excess the distillate will also contain phosphorus pentachloride, which may be removed by redistilling from ordinary phosphorus.

Phosphorus trichloride is a colorless, pungent liquid, boiling at 76° and retaining its liquidity at —115°. Its specific gravity at 0° is 1.613. It fumes in contact with moist air, and is decomposed by water into hydrochloric and phosphorous acids:

$$PCl_3 + 3H_2O = 3HCl + H_3PO_3.$$

Phosphorus pentachloride, PCl_5, is formed by the action of dry chlorine on phosphorus trichloride. This is best accomplished by passing the dry chlorine on the surface of the trichloride by a wide tube, occasionally stirring until the whole solidifies to a crystalline mass. As there is considerable heat developed, the vessel in which the reaction takes place must be kept well cooled.

Phosphorus pentachloride is a yellowish-white, crystalline powder, which fumes strongly on exposure to air, with a very irritating odor. It sublimes at 100° without previously melting; by higher temperatures it is decomposed into phosphorus trichloride and chlorine, the dissociation being complete at 336°. It is decomposed by a small quantity of water into phosphorus oxychloride and hydrochloric acid:

$$PCl_5 + H_2O = POCl_3 + 2HCl.$$

With an excess of water, phosphoric and hydrochloric acids are produced:

$$PCl_5 + 4H_2O = H_3PO_4 + 5HCl.$$
$$POCl_3 + 3H_2O = H_3PO_4 + 3HCl.$$

On account of this affinity for the elements of water, phosphorus pentachloride is a useful laboratory reagent for determining the presence of hydroxyl, especially in organic compounds. For example, the reaction with ethyl alcohol is as follows:

$$C_2H_5.OH + PCl_5 = C_2H_5Cl + POCl_3 + HCl.$$

With acetic acid there is formed acetyl chloride, according to the following reactions:

$$C_2H_3O.OH + PCl_5 = C_2H_3O.Cl + POCl_3 + HCl.$$

With an aldehyde in which the oxygen is united by both its bonds to carbon the following reaction expresses the change:

$$C_6H_5CO.H + PCl_5 = C_6H_5CCl_2.H + POCl_3.$$

Phosphorus tribromide, PBr_3, is prepared like the trichloride, which it closely resembles. It has the specific gravity 2.925 at 0°, and boils at 175°.

Phosphorus pentabromide, PBr_5, resembles the corresponding compound of chlorine in its mode of formation and properties. It is a yellow crystalline solid, which melts below 100° and decomposes into the tribromide and bromine.

A compound of phosphorus with both chlorine and bromine may be formed by bringing together phosphorus trichloride and bromine in the proportion of their molecular weights. The resulting compound is called phosphorus chlorobromide, PCl_3Br_2. It is a yellowish-red, crystalline solid, which decomposes at 35°.

Phosphorus di-iodide, P_2I_4, is prepared by dissolving 41 parts iodine and 5 parts phosphorus in carbon disulphide and cooling, or distilling off the disulphide, when yellow crystals of the di-iodide separate. The crystals melt at 110°, and are decomposed by water into amorphous phosphorus, phosphorous acid, and hydriodic acid:

$$3P_2I_4 + 12H_2O = P_2 + 4H_3PO_3 + 12HI.$$

Phosphorus di-iodide is analogous in composition to liquid hydrogen phosphide, P_2H_4, and to hydrazine, N_2H_4.

Phosphorus tri-iodide, PI_3, is prepared like the preceding compound, using 12 parts iodine to 1 part phosphorus. It is a dark-red, crystalline solid, melting at 55°. It is decomposed by water, as follows:

$$PI_3 + 3H_2O = H_3PO_3 + 3HI.$$

Phosphorus pentafluoride, PF_5, is formed by adding arsenic trifluoride to phosphorus pentachloride:

$$5AsF_3 + 3PCl_5 = 5AsCl_3 + 3PF_5.$$

It is a colorless gas, possessing a density of 62.98. It is decomposed by water into phosphoric and hydrofluoric acids. Its chief use is in the manufacture of a number of compounds of fluorine.

PHOSPHORUS AND OXYGEN.

Two oxides and six acids of phosphorus are known, as follows:

Oxides.	Acids.
	Hypophosphorous acid, H_3PO_2.
Phosphorus trioxide, P_2O_3.	Phosphorous acid, H_3PO_3.
	Hypophosphoric acid, H_2PO_3.
	Metaphosphoric acid, HPO_3.
Phosphorus pentoxide, P_2O_5.	Pyrophosphoric acid, $H_4P_2O_7$.
	Orthophosphoric acid, H_3PO_4.

No oxides have been discovered corresponding to hypophosphorous and hypophosphoric acids; the three acids of phosphoric oxide may be considered as derived by the addition of water, as follows:

$$P_2O_5 \begin{cases} + \; H_2O = 2HPO_3, & \text{Metaphosphoric acid.} \\ + \; 2H_2O = H_4P_2O_7, & \text{Pyrophosphoric acid.} \\ + \; 3H_2O = 2H_3PO_4, & \text{Orthophosphoric acid.} \end{cases}$$

PHOSPHOROUS OXIDE.

Formula, P_2O_3. *Molecular Weight*, 109.14.

This compound is prepared by gently heating phosphorus with incomplete access of air. An imperfect combustion takes place with the formation of the trioxide.

It is a white, amorphous powder, of a garlic-like odor. In contact with air it inflames, forming the pentoxide.

PHOSPHOROUS ACID.

Formula, H_3PO_3. *Molecular Weight*, 81.39.

Preparation.—This acid is formed when phosphorus is exposed to moist air; although in this case it is mixed with hypophosphoric and phosphoric acids. It is prepared pure and in large quantity by leading a stream of chlorine into melted phosphorus under water. Phosphorus trichloride is first produced, which is decomposed, as fast as formed, by the water present:

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

The solution is evaporated until it attains a temperature of 180°, when a thick fluid mass remains, which, on cooling, solidifies to a mass of crystals, having a melting point of 70.1°. On heating above 180° decomposition takes place, with formation of phosphoric acid and hydrogen phosphide, as follows:

$$4H_3PO_3 = 3H_3PO_4 + PH_3.$$

Phosphorous acid is a powerful reducing agent, precipitating gold, silver, and mercury in the metallic state from solutions of their salts.

Phosphites.—The alkali phosphites are all soluble in water, the others are difficultly soluble. The acid is dibasic, one of the three hydrogen atoms not being replaceable by metal. A number of organic salts of phosphorous acid have been prepared, as triethyl phosphite, $(C_2H_5)_3PO_3$. The phosphites are distinguished from the hypophosphites by the former causing precipitates with barium and calcium hydrates.

HYPOPHOSPHOROUS ACID.

Formula, H_3PO_2 (HPH_2O_2). *Molecular Weight*, 65.51.

Preparation.—It is prepared by first making calcium or barium hypophosphite. For pharmaceutical purposes the former of these is preferred, and it is made by boiling phosphorus with calcium hydrate:

$$\underset{\text{Calcium Hydrate.}}{3Ca(OH)_2} + \underset{\text{Phosphorus.}}{2P_4} + \underset{\text{Water.}}{6H_2O} = \underset{\text{Calcium Hypophosphite.}}{3Ca(H_2PO_2)_2} + \underset{\text{Hydrogen Phosphide.}}{2PH_3}.$$

The excess of calcium hydrate is converted into carbonate by carbon dioxide, the solution filtered from the calcium carbonate and a small quantity of phosphate, which is formed at the same time, and the clear filtrate either evaporated for the calcium hypophosphite or decomposed with oxalic acid for the free acid:

$$\underset{\text{Calcium Hypophosphite.}}{Ca(H_2PO_2)_2} + \underset{\text{Oxalic Acid.}}{H_2C_2O_4} = \underset{\text{Hypophosphorous Acid.}}{2H(H_2PO_2)} + \underset{\text{Calcium Oxalate.}}{CaC_2O_4}.$$

When barium hypophosphite is used, sulphuric acid is employed to decompose it.

The calcium oxalate is filtered from the acid and the latter evaporated until it contains 50 per cent. of hypophosphorous acid; in which form it usually comes into the market. The acid may be obtained in the solid form, and nearly absolute, by evaporating carefully at or below 130°, and then placing in a freezing mixture. It melts at 17.4°.

Properties.—When strongly heated hypophosphorous acid is decomposed into orthophosphoric acid and hydrogen phosphide. Solution of hypophosphorous acid decomposes salts of gold, silver, and mercury, with formation of the metal. It is oxidized by chlorine and potassium permanganate.

Acidum Hypophosphorosum Dilutum, U. S. P., contains 10 per cent. by weight of absolute HPH_2O_2.

This acid has a specific gravity of 1.046 at 15°, and the 50 per

cent. acid at the same temperature has a specific gravity of 1.406. The latter is found in commerce.

Impurities and Tests.—The most probable impurities in this acid are hydrochloric, sulphuric, phosphoric, and oxalic acids, and calcium hypophosphite. The acids may all be readily detected by their appropriate tests, and the calcium by the addition of oxalic acid.

Hypophosphites.—The salts of this acid are prepared from the calcium or barium salt by double decomposition. They are all soluble in water.

In the dry state they are quite stable, but in solution they readily undergo change. In pharmaceutical preparations they are usually protected by sugar.

Hypophosphoric Acid, H_2PO_3, is formed with phosphoric and phosphorous acids when phosphorus is slowly oxidized in moist air. By evaporating the solution to a syrupy consistence, and adding cold, saturated solution of sodium acetate, the sodium salt having the formula $NaHPO_3.3H_2O$ separates out. The acid gives a white precipitate with silver nitrate which does not blacken on boiling. This serves to distinguish it from phosphorous and hypophosphorous acids.

PHOSPHORUS PENTOXIDE.

Formula, P_2O_5. *Molecular Weight*, 141.27.

Phosphorus pentoxide, or phosphoric oxide, is prepared by burning phosphorus in dry air or oxygen. It is a bulky, white, amorphous powder, which is capable of being sublimed. It has a powerful affinity for water, hissing when thrown into it. Unless it be rigidly excluded from moist air deliquescence rapidly takes place. On account of this affinity for moisture it is much used in the drying of gases.

ORTHOPHOSPHORIC ACID.

Formula, H_3PO_4. *Molecular Weight*, 97.27.

History.—The existence of this acid was first noticed by Marggraf, in 1746, on account of the peculiar yellow precipitate it produced with silver nitrate. Graham, in 1833, first pointed out the difference between the ortho-, pyro-, and meta- acids.

Occurrence.—The free acid is not known in nature, but in combination with calcium it occurs abundantly in bones, in all vegetable and animal tissues, and in minerals. The deposits of impure calcium phosphate in Southeastern United States and the adjacent islands are the most abundant occurrences as well as sources of this acid in combination.

Preparation.—The use for which the phosphoric acid is in-

tended determines the method of manufacture. For many purposes the acid is made from boneash by treatment with sulphuric acid :

$$\underset{\text{Calcium Phosphate.}}{Ca_3(PO_4)_2} + \underset{\text{Sulphuric Acid.}}{3H_2SO_4} = \underset{\text{Phosphoric Acid.}}{2H_3PO_4} + \underset{\text{Calcium Sulphate.}}{3CaSO_4}.$$

The clear liquid is decanted from the calcium sulphate and evaporated to a small bulk, when, after settling, the supernatant liquid is again decanted from the further deposit of calcium sulphate ; the temperature is then raised to 300°, and maintained at that point until all sulphuric acid is removed. The acid made in this way is useful in the arts and in the manufacture of phosphates.

The official acid is, or should be, prepared directly from phosphorus, by the action of nitric acid. 16 parts of phosphorus are heated in a capacious retort with 100 parts of nitric acid (sp. gr. 1.420), diluted with an equal weight of distilled water. The retort is connected with a condenser, and heat applied until the reaction commences. The heat is then carefully regulated to prevent the action becoming too violent, and, if necessary, distilled water added. The condensed liquid is returned from time to time until the phosphorus is dissolved :

$$\underset{\text{Phosphorus.}}{3P} + \underset{\text{Nitric Acid.}}{5HNO_3} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Phosphoric Acid.}}{3H_3PO_4} + \underset{\text{Nitric Oxide.}}{5NO}.$$

The solution is evaporated at a temperature not exceeding 190°, until the excess of nitric acid is driven off, and a clear, odorless, syrupy liquid remains. Sufficient distilled water is then added to make the liquid weigh 100 parts.

Phosphorus is sometimes contaminated with arsenic, and this should always be removed by diluting the above with one hundred and fifty parts of distilled water, passing in hydrogen sulphide for one-half hour with the liquid at 70°, then removing the heat and continuing the passage of the gas until cold. The liquid is next set aside for twenty-four hours, after which it is filtered and evaporated to 100 parts.

A more expeditious method than this, which has been found to work well on a large scale, was proposed in 1875 by Markoe. 540 parts of distilled water are placed in a large stoneware jar, and the latter set in water. 90 parts of phosphorus are added, then 1 part of iodine, and the whole agitated or stirred in order to bring the iodine and phosphorus in contact. 6 parts of bro-

mine are next run in from a stoppered funnel, drop by drop, in such a way as to bring each drop in contact with the phosphorus and iodine. As soon as the reaction is complete 540 parts of nitric acid (sp. gr. 1.420) are added, and in warm weather a little more water, in order to prevent the action from becoming too violent. The vessel is then covered with a glass or porcelain plate. No further attention is required for from twelve to twenty-four hours. At the end of this time the phosphorus will be found to have disappeared, and the iodine will usually be found sublimed on the lid of the vessel. From this point the process is carried out exactly as in the official method. When the above directions are rigidly adhered to, the operation is an entirely safe one, but in trying to hasten the action by more concentrated solutions explosions have resulted. It is very important to bring every drop of bromine in contact with the phosphorus in order that the reaction may take place before more is added. The iodine is said to modify the action somewhat, but further than that it has no use, for the small amount of bromine is sufficient to act as a carrier of the oxygen from the nitric acid to the phosphorus.

Leaving the iodine out of consideration, since it merely takes the place of a portion of bromine, the reactions involved in the process are, first, the formation of phosphorus pentabromide by the direct union of the elements. This in contact with water is decomposed into phosphoric and hydrobromic acids as follows:

$$\underset{\text{Phosphorus Pentabromide.}}{PBr_5} + \underset{\text{Water.}}{4H_2O} = \underset{\text{Phosphoric Acid.}}{H_3PO_4} + \underset{\text{Hydrobromic Acid.}}{5HBr.}$$

This hydrobromic acid is decomposed by the nitric acid with formation of bromine, water, and nitrogen dioxide, as follows:

$$\underset{\text{Hydrobromic Acid.}}{6HBr} + \underset{\text{Nitric Acid.}}{2HNO_3} = \underset{\text{Bromine.}}{3Br_2} + \underset{\text{Water.}}{4H_2O} + \underset{\text{Nitrogen Dioxide.}}{N_2O_2.}$$

The bromine now combines with a fresh portion of phosphorus, and the reactions are repeated. It is in this way that the small amount of bromine used in the process is able to effect the conversion of a large amount of phosphorus, and without the aid of artificial heat.

When the evaporation is continued in the above process until all water is driven off, the absolute acid remains.

Properties.—Orthophosphoric acid when free from water consists of large, not well defined, rhombic crystals, which melt

at 38.6°. On exposure to moist air, or on the addition of water, they deliquesce to a thick syrupy liquid. The crystals are also easily soluble in alcohol. At temperatures above 200° orthophosphoric acid is converted into the pyro- and meta- varieties.

Acidum Phosphoricum, U. S. P., contains 85 per cent. of absolute H_3PO_4. It has a specific gravity of 1.710 at 15°. "When heated, the liquid loses water; at 200° it gradually begins to change to pyrophosphoric acid. At a still higher temperature it is converted into metaphosphoric acid, which volatilizes in dense fumes, or forms, on cooling, a transparent mass of glacial Phosphoric Acid." A diluted acid is official. It contains 10 per cent., by weight, of absolute acid, and has a specific gravity of 1.057 at 15°.

Impurities.—Phosphoric acid is liable to be contaminated with arsenic, which is detected by hydrogen sulphide, as above directed for the removal of it. When diluted with 5 volumes of water and treated with silver nitrate, the precipitate should not be blackened, indicating the absence of phosphorous acid. A crystal of ferrous sulphate dropped into a mixture of phosphoric and sulphuric acids, should not cause a black color, indicating the absence of nitric acid. No precipitate should be formed, after several hours, by the addition of an equal volume of tincture of ferric chloride, indicating the absence of pyro- and meta-phosphoric acids.

Phosphates.—The salts of this acid usually take the name of phosphates. They are prepared by neutralizing the acid with a hydrate or carbonate. The salts of the alkali metals are soluble in water, the other salts are insoluble in water, but readily soluble in hydrochloric acid. Since the acid is tribasic, there are three classes of salts formed, according as one, two, or three of the hydrogen atoms are replaced by a base. When the acid is neutralized by a carbonate two atoms of hydrogen are replaced.

Detection.—Orthophosphates, as well as the acid, are detected by adding silver nitrate to a neutral solution, when a yellow precipitate forms, consisting of silver phosphate, Ag_3PO_4. This precipitate is soluble in nitric acid and in ammonia. Ammonium molybdate in nitric acid solution causes a yellow precipitate to slowly separate, consisting of ammonium phospho-molybdate, $(NH_4)_3PO_4(MoO_3)_{10}$. In alkaline solutions, magnesia mixture causes a white precipitate of ammonium-magnesium-phosphate, $MgNH_4PO_4.6H_2O$. Phosphoric acid does not coagulate albumen.

PYROPHOSPHORIC ACID.

Formula, $H_4P_2O_7$. *Molecular Weight*, 176.66.

Neither pyrophosphoric acid nor its salts are found in nature.

Preparation.—The acid is prepared by prolonged heating of the orthophosphoric acid to from 200° to 300°, until a portion neutralized with ammonia and treated with silver nitrate yields a pure white precipitate free from yellow color. The sodium orthophosphate, when heated to 240°, is converted into sodium pyrophosphate. By double decomposition between this salt and lead nitrate, lead pyrophosphate is precipitated, which by decomposition with hydrogen sulphide yields the free acid. The acid is also formed when ortho- and meta-phosphoric acids are brought together in molecular proportions in a water-bath.

Properties.—Pyrophosphoric acid exists in the form of crystalline masses. It is easily soluble in water, and in solution it very slowly reverts to the ortho- variety. This may be quickly accomplished by heating.

Pyrophosphates.—The salts of pyrophosphoric acid are called pyrophosphates, and are prepared by heating the orthophosphates to 240°. Two series of salts are formed, those in which two atoms of hydrogen are replaced, and those in which four atoms of hydrogen are replaced by bases.

The pyrophosphates of the alkalies are soluble in water; those of other bases are mostly insoluble in water, but soluble in acids. Solutions of the salts in water remain unchanged, but on boiling with acids or fusing with sodium carbonate they are converted into phosphates.

Detection.—Pyrophosphoric acid and its salts are recognized and distinguished from the other varieties by the white precipitate with silver nitrate, by the absence of a precipitate with ammonium molybdate in the presence of nitric acid, and by the inability of the free acid to coagulate albumen.

METAPHOSPHORIC ACID.

Formula, HPO_3. *Molecular Weight*, 79.39.

This acid is also known as glacial phosphoric acid. It is prepared by heating one of the preceding varieties to redness. It is also produced when phosphorus pentoxide is allowed to slowly melt in cold water.

Properties.—Metaphosphoric acid exists in the form of a white pasty mass. It often contains sodium in the form of sodium metaphosphate, which gives it a more vitreous and transparent appearance. The aqueous solution slowly changes to the ortho- variety, quickly on boiling, and without formation of the intermediate pyro- acid.

Metaphosphates.—The salts of this acid are prepared by heating the ortho- salts to redness. This acid possesses the property of polymerization to such an extent that at least five different series of salts are formed, as follows: RPO_3, metaphosphate; $R_2P_2O_6$, dimetaphosphate; $R_3P_3O_9$, trimetaphosphate; $R_4P_4O_{12}$, tetrametaphosphate; and $R_6P_6O_{18}$, hexametaphosphate.

Detection.—The free acid and its salts are detected and distinguished from the other varieties by the white precipitate with silver nitrate, by

not forming a precipitate with ammonium molybdate in presence of nitric acid, by the free acid coagulating albumen, and by the absence of a precipitate with magnesium sulphate in neutral solution.

PHOSPHORUS WITH OXYGEN AND HALOGENS.

Phosphorus oxychloride, $POCl_3$, is formed by decomposing phosphorus pentachloride with water:

$$PCl_5 + H_2O = POCl_3 + 2HCl.$$

For larger quantities the pentachloride is heated with dry oxalic acid:

$$PCl_5 + H_2C_2O_4 = POCl_3 + 2HCl + CO_2 + CO.$$

Phosphorus oxychloride is a colorless liquid, having the specific gravity 1.711 at 0°. When cooled it solidifies to acicular crystals, which melt at —1.5°. On heating it boils at 107.2°. With water it is decomposed into phosphoric and hydrochloric acids:

$$POCl_3 + 3H_2O = H_3PO_4 + 3HCl.$$

Two other compounds of these elements are known: Pyrophosphoryl chloride, $P_2O_3Cl_4$, a colorless, strongly fuming liquid, boiling between 210° and 215°; and metaphosphoryl chloride, PO_2Cl, a thick, syrupy mass, prepared by heating phosphorus pentoxide and oxychloride to 200°. Phosphorus oxybromide, $POBr_3$, is analogous to the oxychloride and is prepared in a similar manner.

CHAPTER VI.

BORON.

Symbol, B. *Atomic Weight*, 10.9. *Valence*, III.

History.—The element boron was isolated by Gay Lussac and Thénard in 1808, and about the same time independently by Davy. It was known in combination as borax by Geber and the alchemists.

Occurrence.—Boron does not exist in the free state in nature, but is found native in combination with oxygen as boric acid, H_3BO_3, with sodium as borax, $Na_2B_4O_7.10H_2O$, with calcium as borocalcite, $CaB_4O_7.4H_2O$, and with both sodium and calcium as boronatrocalcite, $Na_2B_4O_7.2CaB_4O_7.18H_2O$. It is also found in smaller quantities in a number of other minerals, in sea water, and in the ash of a few plants.

Boron is known in two allotropic modifications. A compound of boron and aluminum, Al_2B_6, was formerly supposed to be the pure element, and bore the name of graphitoidal boron.

1. Amorphous Boron is prepared by heating in a crucible a mixture of 10 parts boron trioxide, B_2O_3, with 6 parts sodium, covered with 5 parts of sodium chloride :

$$B_2O_3 + 3Na_2 = 3Na_2O + B_2.$$

The fused mass, when cold, is treated with diluted hydrochloric acid, which leaves the boron undissolved, as a brown amorphous powder.

This variety is odorless and tasteless, and somewhat soluble in water, imparting to it a yellow color, from which solution it is precipitated unchanged on the addition of an acid. While this variety of boron is permanent in air or oxygen at ordinary temperatures, it readily oxidizes when heated, and may even burn, forming boron trioxide and small quantities of boron nitride, BN ; the latter compound is the result of a union of boron with nitrogen of the air. When air is excluded boron may be heated to whiteness without melting ; fusion may, however, be accomplished by a strong electric current.

Both nitric and hydrochloric acids oxidize boron to boric acid ; and when the element is fused with sodium hydrate, borax is formed.

2. Adamantine Boron. This variety is prepared by fusing boron trioxide with aluminum :

$$B_2O_3 + Al_2 = Al_2O_3 + B_2.$$

The boron cryystallizes as the mass cools and is separated by dissolving the aluminum in sodium hydrate. This variety of boron is in the form of yellow or brownish-yellow crystals, having a specific gravity of 2.68. In this form boron is not pure but contains carbon and aluminum in a proportion corresponding to the formula $B_{48}Al_3C_2$.

The crystals are very hard, being next to the diamond in this respect, and withstand a red heat without change. They are unacted upon by hydrochloric, nitric, or nitrohydrochloric acids. When fused with sodium hydrate they are slowly changed to sodium borate, with evolution of hydrogen. Boron is one of the few elements which unite directly with nitrogen.

BORON AND HYDROGEN.

Boron Hydride, BH_3, is obtained by first fusing together boron trioxide and magnesium, whereby an impure magnesium boride is formed. The fused mass is then treated with diluted hydrochloric acid, when the following reaction takes place :

$$B_2Mg_3 + 6HCl = 3MgCl_2 + 2BH_3.$$

Considerable hydrogen is given off at the same time, but the boron hydride is recognized by its peculiar odor and nauseating effects when inhaled.

It is a colorless gas, which burns with a green flame, yielding boron trioxide and water. The gas is somewhat soluble in water, to which it imparts its peculiar odor.

BORON AND CHLORINE.

Boron Trichloride, BCl_3. When chlorine is passed over amorphous boron, combination takes place with evolution of heat and light. Crystallized boron requires to be heated before combination takes place. In practice dry chlorine is passed over boron trioxide and charcoal, heated to redness :

$$B_2O_3 + 3Cl_2 + 3C = 2BCl_3 + 3CO.$$

The escaping compounds mixed with some chlorine are passed through a freezing mixture, by which the boron trichloride is condensed. The latter is then finally freed from chlorine by agitation with and distillation from mercury.

Properties.—Boron trichloride is a colorless, mobile, strongly refracting liquid. Its specific gravity at 17° is 1.35. On the application of heat it boils at 18.23°. It fumes in the air, and is decomposed by water into hydrochloric and boric acids.

BORON AND OXYGEN.

BORON TRIOXIDE.

Formula, B_2O_3. *Molecular Weight*, 69.44.

Preparation.—This oxide is formed when boron is burned in air or oxygen, but it is usually prepared by heating boric acid to redness:

$$2H_3BO_3 = B_2O_3 + 3H_2O.$$

The liquid should be poured out into thin layers and, when cold, broken into pieces of suitable size.

Properties.—Boron trioxide, when first prepared, is a colorless, transparent, vitreous solid, becoming opaque when exposed to air, owing to absorption of moisture. Its specific gravity at 4° is 1.83. At a white heat it is volatilized.

BORIC ACID.

Formula, H_3BO_3. *Molecular Weight*, 61.54.

History.—This acid was first prepared and used in 1702 by Homberg, who obtained it by treating borax with a mineral acid. It was known under the name of sedative salt, or *sal sedativum Hombergii*. In 1774, Höfer, a Florentine apothecary, discovered the acid in the waters of the Tuscan lagoons, and some years later manufactories were established for its preparation, but were not successful until 1828, when the escaping jets of steam in the vicinity were utilized in the evaporation of the water.

Occurrence.—Boric acid occurs in the free state in nature. In the volcanic districts of Tuscany there are found numerous jets of steam issuing from crevices in the ground termed *suffoni* or *fumeroles*. This steam contains considerable quantities of boric acid. The number of these jets is often increased by boring. Boric acid is also found in considerable quantity combined with sodium, as borax, or tincal, on the borders of certain lakes in Thibet and Persia. Borax is also found in Clear Lake and Death Valley in California, and near Pyramid Lake in Nevada. The acid is further found in the mineral borocalcite, as calcium borate, in the nitre beds of Peru, and in some other districts combined with both sodium and calcium as boronatrocalcite.

Preparation.—A number of the fumeroles are surrounded by a wall of solid masonry and the enclosure filled with water, which condenses the steam and becomes charged with boric acid, at the same time the water is heated and evaporates.

In the United States so much borax is found that it has been used for furnishing the acid by decomposition with hydrochloric acid:

$$Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3.$$

This is effected by dissolving 1 part of borax in 2½ parts of boiling water and adding an excess of strong hydrochloric acid. On cooling, the boric acid crystallizes out and is purified by recrystallization.

Properties.—Boric acid (**Acidum Boricum**, U. S. P.) consists of "transparent, colorless scales, of a somewhat pearly lustre, or, when in perfect crystals, six-sided, triclinic plates, slightly unctuous to the touch, odorless, having a faintly bitterish taste, and permanent in the air." Its specific gravity at 15° is 1.4347. It is soluble in 25.6 parts of water, and in 15 parts of alcohol at 15°; in 3 parts of boiling water and in 5 parts of boiling alcohol. The alcoholic solution burns with a green flame.

Glycerin is also an excellent solvent for boric acid, 1 part of the acid dissolving in 10 parts of this solvent. The preparation known as boroglycerin is made by dissolving 62 parts of boric acid in 92 parts of glycerin at a temperature of 150°, and maintaining that heat until the mixture weighs 100 parts.

At 100° boric acid loses one molecule of water and is converted into metaboric acid, HBO_2. The latter is a white powder, and is slowly volatilized when maintained at the above temperature for a long time. When boric acid is kept at a temperature of 160° for some time, pyroboric acid ($H_2B_4O_7$) is produced, according to the following reaction:

$$4H_3BO_3 = H_2B_4O_7 + 5H_2O.$$

It is a brittle, vitreous mass, and is also known under the name of tetraboric acid.

Boric acid forms weak combinations with phosphoric, sulphuric, and some other acids, which indicate that it sometimes plays the part of a base. "The aqueous solution of boric acid colors blue litmus paper red, but yellow turmeric paper brownish-red after drying, even when the solution has been acidulated with hydrochloric acid; this brownish-red color is changed to bluish-black by ammonia water."

Impurities and Tests.—The most probable impurities are chloride and sulphate of sodium, and certain metals derived from the vessels used in the process of manufacture, like copper, lead, and iron. Chlorides may be detected by silver nitrate forming a

white precipitate insoluble in nitric acid, sulphates by an equally insoluble precipitate with barium chloride, and the metals by a blackening with ammonium sulphide.

The most characteristic test for the acid is the green color it imparts to the flame of its alcoholic solution.

Borates.—Boric acid is tribasic, and its salts are very unstable; the best known one is magnesium borate, $Mg_3(BO_3)_2$. It, however, forms a number of salts with organic bases. The compounds of a few bases with metaboric acid are more stable, although not used or well known. The most familiar borates are those of pyroboric acid, which are very stable, and one of them, borax, $Na_2B_4O_7$, is extensively used.

Borax possesses the ability, when fused with different metallic oxides, of forming double salts of characteristic colors. It is on this property that the use of borax in blowpipe analysis depends, since by their action and color when brought into a borax bead on the end of a platinum wire many metals are detected.

Boron Trisulphide, B_2S_3, is formed when sulphur vapor is passed over heated amorphous boron; or a more practical method is to pass the vapor of carbon disulphide over a heated mixture of boron trioxide and charcoal:

$$2B_2O_3 + 3CS_2 + 3C = 2B_2S_3 + 6CO.$$

Boron trisulphide is a yellowish-white, friable, vitreous solid, easily decomposed by water into hydrogen sulphide and boric acid:

$$B_2S_3 + 6H_2O = 2H_3BO_3 + 3H_2S.$$

Boron Nitride, BN, is prepared by the direct union of amorphous boron and nitrogen at a white heat. This is interesting because of the indisposition of nitrogen to combine directly with any other element. Boron nitride is prepared more economically by heating to redness, in a platinum crucible, a mixture of one part anhydrous borax and two parts of dry ammonium chloride:

$$Na_2B_4O_7 + 4NH_4Cl = 2NaCl + 4BN + 2HCl + 7H_2O.$$

The fused mass is washed with water and hydrochloric acid, to remove the salt and some boric acid, which is mixed with the nitride.

Boron nitride is a white, light, amorphous powder, which phosphoresces in a gas flame with a greenish-white light. It is decomposed when heated in a current of steam into boric acid and ammonia:

$$BN + 3H_2O = H_3BO_3 + NH_3.$$

Boron nitride is infusible and unchanged, even at the melting point of nickel. It is not affected by nitric or hydrochloric acids, nor by alkaline solutions. Chlorine has no effect on it at a red heat. On fusion with potassium hydrate it evolves ammonia.

CHAPTER VII.

THE CARBON GROUP.

SILICON.

Symbol, Si. *Atomic Weight*, 28.2. ***Valence*, IV.**

History.—The oxide of this element was early recognized as a distinct substance. Berzelius, in 1810, first isolated the element by fusing together iron, carbon, and silica. The crystallized variety was prepared by Deville in 1854, and its properties were investigated by himself and Wöhler.

Occurrence.—Next to oxygen, silicon is the most abundant element known. It is not found in the free state, but in combination with oxygen in quartz it is widely distributed. It is, further, the chief constituent of nearly all rocks, and consequently, also, of the soils which have resulted from the decomposition of rocks. It is also found in the ashes of many plants, having assisted to make up their mineral structure. Silicon exists in two allotropic conditions, the *amorphous* and the *crystalline*.

Preparation.—Amorphous silicon is best prepared by mixing equal parts of powdered and well-dried white sand (SiO_2) and magnesium. This mixture is placed in a test-tube and heated with a Bunsen flame. The reaction soon begins with a glowing which rapidly extends throughout the entire mass. The cooled, hardened product is powdered and washed with dilute hydrochloric acid to remove the magnesium oxide. The product is an amorphous, brown powder, which, when heated in the air, ignites and burns with the formation of the dioxide, SiO_2.

Silicon is insoluble in water and acids, except hydrofluoric, which dissolves it readily.

The crystalline variety is prepared by throwing, in small portions at a time, into a red-hot Hessian crucible a mixture of 15 parts of potassium silico-fluoride and 5 parts of sodium, then 36 parts of granulated zinc are quickly added, and the mass is covered with sodium chloride. The crucible is then maintained at a temperature just below the boiling point of zinc (1040°) for some time. The cooled mass is treated successively with hydrochloric, boiling nitric, and hydrofluoric acids, which leaves the

crystals of silicon undissolved, as these are distinctly more refractory than the amorphous variety.

Properties.—When thus prepared, silicon is in the form of dark, lustrous, octohedral crystals, with a specific gravity of 2.49, and a degree of hardness sufficient to scratch glass. They withstand a white heat without igniting, and resist the action of all acids, except a mixture of hydrofluoric and nitric, which, when hot, dissolves them slowly. Hot concentrated solution of sodium hydrate dissolves silicon with formation of sodium silicate and evolution of hydrogen.

Silicon Hydride, SiH_4, is prepared by treating magnesium silicide with hydrochloric acid:

$$Mg_2Si + 4HCl = 2MgCl_2 + SiH_4.$$

The magnesium silicide is prepared by fusing together 40 parts of anhydrous magnesium chloride, 35 parts of dried sodium silicofluoride, 10 parts of fused sodium chloride, and 20 parts of sodium.

Silicon hydride is a colorless gas, which may be collected over water or mercury. When pure, the gas does not inflame spontaneously, but if mixed with hydrogen or warmed, it takes fire. In burning it evolves dense fumes of silicon dioxide, SiO_2, with formation of water at the same time. When mixed with chlorine, it explodes spontaneously.

Silicon Tetrachloride, $SiCl_4$, may be formed by burning silicon in chlorine, but is usually prepared by heating a mixture of silicon dioxide and carbon in a current of chlorine:

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO.$$

Silicon tetrachloride is a colorless, fuming liquid, having the specific gravity, at 0°, of 1.52, and boiling at 59.5°. It is decomposed by water into hydrochloric and silicic acids:

$$SiCl_4 + 4H_2O = H_4SiO_4 + 4HCl.$$

Silicon Hexachloride, Si_2Cl_6, is formed in small quantity when the vapor of silicon tetrachloride is passed over silicon heated to 1000°. It is a colorless, fuming liquid, which solidifies at —1°, and boils at 146°. Its specific gravity is 1.58 at 0°. It possesses the peculiarity of decomposing between 350° and 1000°, while above the latter and below the former temperature it is stable.

Silicon Chloroform, $SiHCl_3$, is produced when silicon is heated to redness in a stream of hydrochloric acid gas:

$$Si + 3HCl = SiHCl_3 + H_2.$$

It is a colorless, inflammable liquid, burning with a green-edged flame.

Silicon Bromoform, $SiHBr_3$, and Silicon Iodoform, $SiHI_3$, have also been prepared.

Silicon Tetrabromide, $SiBr_4$, is produced by passing bromine vapor over silicon dioxide and carbon, heated to low redness.

It is a colorless, heavy, oily liquid, which at 13° solidifies to a crystalline mass. It boils at 154°, and has a specific gravity of 2.81. It is decomposed into silicic and hydrobromic acids on the addition of water.

Silicon Hexabromide, Si_2Br_6, is a crystalline compound, prepared similarly to silicon hexachloride. It readily melts on the application of heat and boils at 240° without decomposition.

Silicon Tetraiodide, SiI_4, is prepared by passing vapor of iodine mixed with carbon dioxide over red-hot silicon. The carbon dioxide carries off the vapor of the tetraiodide as fast as formed and thus prevents its decomposition.

Silicon tetraiodide is a colorless, crystalline solid, soluble in carbon disulphide, and decomposed by water into silicic and hydriodic acids.

Silicon Hexaiodide, Si_2I_6, is formed by heating the tetraiodide with silicon to 280°. It is a crystalline solid, which fuses with decomposition at 250°, and is decomposed by water.

Silicon Tetrafluoride, SiF_4, is prepared by heating silicon dioxide with fluor spar and sulphuric acid:

$$SiO_2 + 2CaF_2 + 2H_2SO_4 = SiF_4 + 2CaSO_4 + 2H_2O.$$

Silicon tetrafluoride is a colorless, very pungent gas, which, under a pressure of thirty atmospheres or at a temperature of —107°, condenses to a liquid and at still lower temperatures solidifies. It is decomposed by water into silicic and hydrofluosilicic acids:

$$3SiF_4 + 4H_2O = H_4SiO_4 + 2H_2SiF_6.$$

Hydrofluosilicic acid, H_2SiF_6, is formed when the vapor of silicon tetrafluoride is led into water. The gelatinous silicic acid, which separates at the same time, would quickly stop the tube, if it were not prevented by keeping the latter under mercury, on the surface of which is placed the water. Each bubble of escaping gas forms a mass of silicic acid as it enters the water from the mercury. The hydrofluosilicic acid is obtained in aqueous solution, which fumes in contact with the air, and is decomposed by boiling into silicon tetrafluoride and hydrofluoric acid. It is useful as a laboratory reagent, since it forms a number of insoluble salts termed hydrofluosilicates, among which are those of potassium, lithium, and barium.

SILICON DIOXIDE.

SILICA.

Formula, SiO_2. *Molecular Weight,* 59.96.

This compound of silicon is the most abundant of all those in which the element occurs. There are three well-defined varieties of silica. Two of them are crystalline and one is amorphous. The most abundant of these is represented by *quartz.*

which, when pure, consists of colorless, transparent, hexagonal crystals, having a specific gravity of 2.6, and represented in the scale of hardness by 7. It is sometimes slightly colored, as in amethyst, smoky quartz, and rose quartz.

Many of our most abundant rocks, as granite, gneiss, and syenite, are made up chiefly of quartz. It is also largely represented in sand and sandstone.

The second variety, also crystalline, is known as *tridimite*, which was originally found in Mexico, but is also distributed through a number of trachytic rocks. It occurs in hexagonal plates, having a specific gravity of 2.3, and a hardness the same as quartz.

The third variety is amorphous, the type of which is *chalcedony*. It has a specific gravity of 2.3. This variety frequently occurs with varying amounts of coloring impurities, as shown in *agate*, *jasper*, and *flint*. The precipitated silica formed when silicon fluoride is passed into water and dried, or when a soluble silicate is treated with an acid, the precipitate collected and dried, also belongs to this variety. In this form it possesses a specific gravity of 2.2 ; if, however, it be strongly heated for some time the specific gravity becomes 2.3. The quartz crystal likewise changes in specific gravity, when finely powdered and heated, from 2.6 to 2.3. An amorphous form known as *kiesel guhr*, or diatomaceous earth, occurs in large deposits near Berlin, Germany, and in several localities in the United States. *Opal* is a hydrated silicic oxide, as is also *geyserite*. Silicon dioxide is also found widely distributed in the vegetable and animal kingdoms, although not in such large amounts as among minerals. In the stalks of various grasses, and in the hair of man and animals, it is an important constituent.

The silicified wood found in many localities, but especially in the vicinity of the Yellowstone National Park in this country, is formed by silicon replacing the carbon of the wood.

All the varieties of silica are insoluble in water and acids, except in hydrofluoric acid, which dissolves them all. Quartz, even in fine powder, is practically insoluble in boiling solutions of the alkaline hydrates or carbonates, while the other two varieties will dissolve, the amorphous variety completely. This serves to distinguish quartz from the other two. All varieties on fusing with dry sodium or potassium carbonate form soluble silicate of the alkali :

$$SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2.$$

On treating this solution of sodium silicate with acid, evaporating to dryness, adding water, collecting the precipitate, and washing thoroughly with boiling water, the purest amorphous silica is obtained.

All varieties of silica are extensively used by man. Quartz crystal and sand are largely used in the manufacture of pottery and glass; many of the colored varieties are used as gems; the amorphous kiesel guhr is employed as an absorbent of nitroglycerin, forming dynamite; and agate, on account of its hardness, goes to make mortars for the use of chemists.

Silicic Acid, H_4SiO_4. When hydrochloric acid is added to a dilute solution of sodium silicate, no precipitate occurs. If this solution be submitted to dialysis the sodium chloride and excess of hydrochloric acid will pass through, while a transparent colorless solution remains, supposed to contain orthosilicic acid, H_4SiO_4. This solution may be concentrated until it contains 14 per cent. of silica; a further concentration causes it to solidify into a jelly-like mass. This acid is represented in a few silicates, as *olivine*, Mg_2SiO_4, and *zircon*, $ZrSiO_4$. When the above clear solution of silicic acid is evaporated in a vacuum at 15°, a glass-like residue remains, supposed to consist of metasilicic acid, H_2SiO_3; on drying these two acids at a higher temperature silicon dioxide and water result:

$$H_4SiO_4 = H_2O + H_2SiO_3.$$
$$H_2SiO_3 = H_2O + SiO_2.$$

A large number of metasilicates are known, a very abundant one being *enstatite*, $MgSiO_3$. The best known one is perhaps sodium silicate, Na_2SiO_3. A number of silicates occur in which the base is combined with a multiple of the formula possessed by the above acid, with various proportions of water. Such compounds are known as *polysilicates*, and make up the large number of naturally occurring silicates.

Silicates.—Apart from those silicates occurring native and those manufactured for special purposes, like glass, we have one official, namely, sodium silicate, or soluble glass, **Liquor Sodii Silicatis.** This is prepared by fusing together sodium carbonate and sand, and allowing the resulting liquid mass to run into water, which causes it to solidify in smaller and more porous pieces, so that it may afterward be more easily dissolved in water. It is found in commerce in almost all degrees of concentration, from a thin, transparent liquid to a thick gelatinous mass. The

U. S. P. directs that which has a specific gravity of 1.3 to 1.4. This strength contains from 10 to 12 per cent. of sodium and 20 to 24 per cent. of silica. It is used largely in bandaging.

Glass.—When sand, lime, and potassium carbonate are fused together in proper proportions a transparent, insoluble substance results, known as glass. Bohemian glass is a silicate of potassium and calcium. It is very difficult to fuse, and resists the action of most chemicals. Crown or window glass is a silicate of calcium and sodium with small quantities of aluminum and iron. Bottle or green glass is similar in composition with less sodium and more calcium. It also contains more iron. Flint glass is a silicate of potassium and lead. It is quite fusible, and is chiefly valuable on account of its high refractive power, which makes it applicable in the manufacture of lenses.

Detection.—Soluble silicates are detected by the gelatinous precipitate that is produced on the addition of an acid ; and both soluble and insoluble silicates are recognized by means of the salt of phosphorus bead, which, when held in the blowpipe flame with silica or a silicate, becomes opaque and is found to contain a floating mass, known as the *silica skeleton.*

Silicon Disulphide, SiS_2. When a mixture of silica and carbon is heated to whiteness, and vapor of carbon disulphide led over it, there are formed long, silky crystals of the above compound, which decompose on the addition of water into hydrogen sulphide and silicic acid.

Silicon Carbide, SiC. This compound is known as carborundum, and has come into use as a polishing agent because of its excessive hardness, which is said to equal that of the diamond. It is made by heating a mixture of carbon, sand, and salt in an electric furnace.

CARBON.

Symbol, C. *Atomic Weight*, 11.90. *Valence*, IV.

History.—Carbon in the form of charcoal has been known from the earliest times. Graphite was thought to be identical with molybdenite, and the diamond was supposed to be a kind of quartz crystal. In 1779 Scheele pointed out the difference between molybdenite and graphite, and concluded that the latter must be looked upon as a kind of mineral coal. Numerous experiments were carried out in the latter half of the last century to determine the composition of the diamond.

A number of investigators subjected it to high temperatures and observed that it disappeared, and, at the suggestion of Lavoisier, a diamond in a glass vessel over mercury was ignited by

means of a burning-glass, and the fact noted that carbon dioxide was produced. Davy, some years later, combined the carbon dioxide produced by the combustion of a diamond with calcium, and by reducing the calcium carbonate obtained pure carbon.

Occurrence.—Carbon exists in the free state in nature in three allotropic modifications,—crystallized, as *diamond* and *graphite*, and amorphous, as *coal*. Diamonds are found in Brazil, Georgia, California, New South Wales, and South Africa.

Graphite is distributed throughout the world. A very good quality is found in the North of England. Large deposits occur in Germany, in Southern Siberia, in Ceylon, at Ticonderoga, in New York, at Sturbridge, in Massachusetts, and at Sonora, in California.

Coal is found in nearly all parts of the world.

In combination, carbon is found in petroleum and in natural gas, in nearly all vegetable and animal matter, and, combined with calcium as carbonate, in marble, limestone, and chalk.

(1) Diamond. Diamonds occur either in alluvial deposits, supposed to have resulted from the decomposition of certain kinds of micaceous rock, or else loose in sand. When found they are usually covered with an opaque layer. This surface is removed and the gem given a great number of faces by cutting and polishing. These faces are so formed as to reflect the greatest amount of light. This is accomplished by so arranging the back planes or faces that nearly all the light strikes them at an angle greater than 24° 13′, when it is all reflected. Diamond dust is used in the cutting and polishing.

The diamond belongs to the regular or isometric system of crystallization, the prevailing form being the octohedron. It has a specific gravity of 3.5 to 3.6, and is the hardest substance known, being rated as 10 on the scale of hardness. It is insoluble in all known liquids.

The weight of the diamond is usually stated in carats, a carat being equal to 3.17 grains, or 0.204 gramme. A variety of black diamond from Brazil, which is worthless as a gem, is much used in drilling rocks. The specific gravity of the black variety is less than that of the transparent one, being about 3.0.

On the application of heat diamonds remain unchanged in an atmosphere of hydrogen or when air is excluded, even at a white heat; but the intense temperature of the electric current causes them to swell to a mass of coke or graphite. At these temperatures in air or oxygen combustion takes place, carbon dioxide

being formed, and a small quantity of ash remaining. This ash, which consists of silica and ferric oxide, amounts to from 0.05 to 0.20 per cent.

The diamond is a poor conductor of electricity and heat.

The clearest specimens of the diamond become of great value when properly cut and polished. One of the finest is the "Pitt" or "Regent" diamond, which weighs 136 carats and is valued at $600,000. A number of larger ones have been found, but the weight after cutting rarely exceeds 250 carats.

(2) Graphite. This substance, which is also known as plumbago or black lead, occurs in crystalline form, not well defined, but frequently approaching hexagonal prisms. It may also be made artificially by adding to melted cast-iron a considerable quantity of charcoal, which on cooling is deposited as crystals of graphite.

Graphite possesses a black metallic lustre. It feels soft and greasy between the fingers, and leaves a black mark when drawn across paper. Its specific gravity varies from 1.84 to 2.50. On the application of heat it remains unchanged, when air and oxygen are excluded, but at very high temperatures, in a stream of oxygen, it is slowly consumed, with more difficulty, however, than the diamond.

The amount of ash which remains on ignition is variable, being from 1 to 10 per cent. In the purer varieties there are also present from .5 to 1.3 per cent. of hydrogen.

Graphite is purified by digesting 1 part, on a water-bath at 60°, with 3 parts of potassium chlorate, and sufficient nitric acid to render the mixture fluid, or the graphite is allowed to stand for twenty-four hours with a mixture of potassium chlorate and sulphuric acid. The product is washed with water and heated, when it swells up with a violent evolution of gas, and there finally results a very fine powder of pure graphite. Hydrofluoric acid is sometimes used in the purification, in order to dissolve and render volatile the silica.

Graphite when mixed with fire clay is used for making the black-lead or plumbago crucibles. It is also useful as a polishing agent and in the manufacture of lead-pencils. For this latter purpose the purified powder is mixed with a fine clay, and by the aid of water made into a plastic mass. The mixture is then forced through small holes by powerful pressure, which gives the leads the desired shape. The long cylinders are then cut into the required lengths and enclosed in wood.

(3) Amorphous Carbon. Under this head may be included the following varieties: (*a*) Gas carbon, (*b*) Coke, (*c*) Wood charcoal, (*d*) Animal charcoal, (*e*) Lampblack.

(*a*) Gas carbon is found in the upper part of the retorts in which coal is heated in the preparation of illuminating gas. It occurs in iron-gray masses of a metallic lustre, and possesses considerable hardness. It varies in specific gravity from 1.75 to 2.50, according to the distance from the surface of the retort. It is a good conductor of electricity, and is used for the carbon plates in several forms of batteries. Sometimes it is used for the carbon pencils in the arc electric light.

(*b*) Coke is a by-product in the manufacture of illuminating gas. It remains in the retort after the volatile portions, which go to make gas, have been driven off by destructive distillation. Large quantities of coal in the United States are converted into coke in special coking ovens and the volatile products allowed to escape. The answer to the inquiry about the wastefulness of the process is that the coke is more valuable than the coal, and there is not the demand for the volatile products to make it remunerative to retain them.

Coke occurs in irregular, brittle, porous masses, of a grayish, somewhat metallic lustre. It does not burn so easily as coal, and requires a constant draught of air. Its combustion is attended with great heat and but little smoke. It is extensively used in metallurgical operations. The composition of coke is about 91 per cent. pure carbon, 5 to 6 per cent. of ash, with varying proportions of oxygen, hydrogen, and nitrogen.

(*c*) Wood charcoal usually goes under the simple name of charcoal. Pure charcoal is obtained when sugar is burned in a platinum or porcelain dish, and it is purified in a current of chlorine. It is tasteless, insoluble, conducts electricity, and has a specific gravity of 1.57.

Wood charcoal is prepared by the incomplete combustion of wood. This is accomplished by covering piles of wood with earth and igniting at suitable openings. By regulating the access of air slow combustion takes place, water, some carbon dioxide, and various other products escape, and charcoal remains. In the preparation of wood alcohol and acetic acid the process of charring wood is carried out in large iron retorts, so that the volatile products are saved. It has been found, however, that a temperature below that necessary to produce charcoal is best for preparing the volatile products.

The yield of charcoal is from 17 to 20 per cent. when made in the ordinary way, but by the use of super-heated steam to regulate the temperature, and maintaining it at 300°, the yield may be increased to 33 per cent. The proportion of carbon in the product, however, is diminished, being only about 65 per cent., while the oxygen, hydrogen, and nitrogen are correspondingly increased. By increasing the temperature to 400° the yield is decreased to 20 per cent., and the carbon in the product increased to 80 per cent. At 1000° the yield is 18.7 per cent., and the carbon in the product 82 per cent. A larger yield is obtained when the process is carried out slowly and when the wood is dry.

The most esteemed charcoal for pharmaceutical purposes is prepared from willow twigs two or three years old. It is official as **Carbo Ligni,** U. S. P.

The best charcoal is hard and brittle, breaking with a lustrous fracture and emitting a metallic sound when struck. As ordinarily prepared it is a poor conductor of heat and electricity, but when prepared at a high temperature it is more compact and becomes a better conductor. Like all other varieties of carbon, it is infusible. Wood charcoal possesses in a marked degree the power to absorb and condense gases. One volume of boxwood charcoal was found by Hunter to absorb the following volumes of gases under ordinary pressure and at a temperature of 0° :

	Volumes.		Volumes.
Hydrogen	4.4	Nitric oxide	70.5
Nitrogen	15.2	Ethene	74.4
Oxygen	17.9	Nitrous oxide	86.3
Carbon monoxide	21.2	Cyanogen	107.5
Carbon dioxide	67.7	Ammonia	171.7

On account of this property charcoal becomes valuable for absorbing noxious gases and destroying them. It also possesses the power of decolorizing dark liquids, although not in the same degree as the next variety.

(*d*) Animal charcoal is prepared by charring bones and other animal matter. The variety known as bone-black is formed when bones are heated in closed iron retorts ; the by-product in this case is "Dippel's animal oil." Animal charcoal is official in two forms, **Carbo Animalis,** U. S. P., and **Carbo Animalis Purificatus,** U. S. P. The crude article is in dull-black, granular fragments or powder ; it is odorless and tasteless and insoluble in water or alcohol. When ignited it should leave about 86 per cent. of a white ash, consisting of calcium phosphate and

carbonate, which should be completely soluble in hydrochloric acid with the aid of heat. The purified animal charcoal is prepared by digesting in a water-bath for twenty-four hours two parts of the crude preparation with three parts of hydrochloric acid and fifteen parts of water, washing, drying, and heating to dull redness.

When purified, animal charcoal is a dull-black powder, odorless, tasteless, insoluble in water and all other solvents. When ignited at a high temperature, with a little mercuric oxide and free access of air, it should leave only a trace of residue. Purified animal charcoal possesses the power of absorbing coloring matter from solution. It will withdraw the color from solutions of indigo or logwood, and remove the fusel oil from alcohol. It absorbs alkaloids and astringent compounds from their solutions, and gives them up to boiling alcohol. Many of the domestic filters for the purification of water are constructed of animal charcoal and sand. Perhaps the most extensive application of animal charcoal is in the decolorizing of sugar, and in the purification of the heavy portions of petroleum, by which such preparations as petrolatum are made.

(*e*) Lampblack. This variety of carbon is in very fine powder. It is obtained from the smoky flame of many bodies rich in carbon, as resins, when their combustion takes place without much access of air, and the products are condensed. This condensation is accomplished by passing the products through a series of chambers. Rosin and petroleum are most frequently employed in the preparation of lampblack, but the product is not pure. The purification is effected by heating for some time in a current of chlorine. A very pure lampblack is made from the natural gas of Western Pennsylvania and Ohio. The product from this last source is very pure and is sometimes known under the name of *diamond black*. Lampblack, when pure, is a velvety black, impalpable powder, having a specific gravity of 1.729 at 17°. It should mix readily with water, and yield no color to alcohol and ether when agitated with them, showing the absence of oily impurities. It is used to give a black color to paints and inks, not only on account of its intense black color, but also because of its indestructibility.

COAL.

Coal is classified as a variety of carbon, although it contains, besides that element, considerable quantities of oxygen, hydrogen, nitrogen, mineral matter, and frequently sulphur.

Our present supply is the product from the decomposition of plants of a former age, this decomposition having taken place under great pressures without access of air, and in the presence of moisture.

Owing to the differences under which their formation took place, we have several different varieties of coal. They may, however, be arranged into two classes, *Anthracite* and *Bituminous* coals.

Anthracite is found in this country most abundantly in Pennsylvania, and in lesser amount in Rhode Island. An inferior variety is found in Wales, France, Saxony, and Southern Russia. It contains about 90 per cent. of carbon and only very small quantities of sulphur. It is hard, with a conchoidal fracture and an iron-black color, frequently displaying iridescence. It burns with but little flame and gives out an intense heat. The volatile matter is contained in it in small amount, being from 6 to 7 per cent.

Bituminous coal is found in all parts of the world. It is much softer than anthracite, and contains a larger proportion of volatile matter. It is used extensively in producing coke and in the manufacture of illuminating gas, in which process it yields many useful by-products.

Cannel coal is a variety of this class which, on account of its large proportion of volatile matter, is much used in England for gas making. The carbon of bituminous coal varies from 70 to 91 per cent., the sulphur from 0.40 to 2.25 per cent., the nitrogen from 1.00 to 2.50 per cent., and the ash from 0.75 to 20 per cent.

Lignite is a brown coal of more recent formation than the two preceding varieties. It frequently retains the structure of the wood from which it was formed.

Jet is a variety of this brown coal, so compact as to take a fine polish.

CARBON AND HYDROGEN.

These two elements unite directly with each other, although with some difficulty and always under peculiar conditions. The number of such compounds, mostly formed by indirect means, however, is very great. These compounds of carbon and hydrogen, when associated with oxygen and nitrogen, become well-nigh innumerable, and make up the material of *Organic Chemistry*.

The subject of organic chemistry, therefore, is confined to the

consideration of the compounds of carbon and their derivatives, and the classification of these is based on several series of *hydrocarbons*, or compounds of carbon and hydrogen.

It will be sufficient at this point to give some description of two or three compounds of these two elements in order to have them for comparison with the hydrogen compounds of the preceding elements.

METHANE.

MARSH GAS.

Formula, CH_4. *Molecular Weight*, 15.90.

Marsh gas is the first member of the *paraffin series* of hydrocarbons. It occurs free in nature wherever vegetable matter is undergoing decomposition in the presence of moisture. This is always noticeable where leaves and other vegetable matter are under water, and the bubbles which rise when such a mass is disturbed are composed chiefly of this gas. It also occurs in coal seams, giving rise to the *fire damp* of the miners, and is the explosive element in mine disasters. The very lightest part of petroleum consists largely of this gas, and escapes as soon as the oil is relieved of its pressure on coming to the surface. Closely associated with this is the *natural gas*, which has marsh gas for its chief constituent. Natural gas is found in great abundance in Pennsylvania, Ohio, West Virginia, and Indiana. In all these places it has been successfully used for heating, and, after treatment, also for lighting. It has been found especially valuable in metallurgical operations. The supply, which at first seemed inexhaustible, has in the past few years perceptibly diminished, and it is only a question of some years more, in many localities, when a return will be made to other fuels.

Preparation.—Marsh gas may be prepared by heating sodium acetate and hydrate in an iron or copper retort, when the following reaction takes place :

$$\underset{\text{Sodium Acetate.}}{NaC_2H_3O_2} + \underset{\text{Sodium Hydrate.}}{NaOH} = \underset{\text{Sodium Carbonate.}}{Na_2CO_3} + \underset{\text{Marsh Gas.}}{CH_4}.$$

In practice it is preferable to substitute calcium oxide for a part of the sodium hydrate, thereby preventing the mixture from liquefying. This is best accomplished by using sodium acetate, 1 part, and soda-lime, 4 parts. Soda-lime is made by slaking calcium oxide with a solution of sodium hydrate of such strength that 2 parts of calcium oxide shall be mixed with 1 part of

sodium hydrate. The mixture is then dried and heated in an iron or Hessian crucible, after which it is preserved in a tightly-closed bottle.

Marsh gas may be obtained absolutely pure by adding zinc methyl to water:

$$\underset{\text{Zinc Methyl.}}{Zn(CH_3)_2} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Zinc Hydrate.}}{Zn(OH)_2} + \underset{\text{Marsh Gas.}}{2CH_4}.$$

Another method of preparation consists in passing a mixture of carbon disulphide vapor and hydrogen sulphide over red-hot metallic copper:

$$\underset{\text{Hydrogen Sulphide.}}{2H_2S} + \underset{\text{Carbon Disulphide.}}{CS_2} + \underset{\text{Copper.}}{8Cu} = \underset{\text{Copper Sulphide.}}{4Cu_2S} + \underset{\text{Marsh Gas.}}{CH_4}.$$

This process is of interest because of the fact that every one of the compounds employed is strictly inorganic and may be made directly from elementary matter, thus rendering it possible to prepare many of what are considered organic compounds synthetically.

Properties.—Marsh gas is colorless, odorless, and tasteless, and is insoluble in water. At a pressure of 54.9 atmospheres and a temperature of —81.8° the gas liquefies. This liquid commences to boil at —164° under ordinary atmospheric pressure. Marsh gas is combustible, and when mixed with 2 volumes of oxygen or 10 volumes of air it explodes with considerable violence. By the electric spark the gas is slowly decomposed into its constituent elements. When a mixture of 1 volume of marsh gas and 2 volumes of chlorine is exposed to direct sunlight or the flame of a taper, a sudden reaction takes place, with the formation of hydrochloric acid, and the separation of carbon as a black, very finely divided powder. Marsh gas is not considered poisonous, since when mixed with air to the extent of 9 per cent. it has been inhaled by workmen in coal mines without serious inconvenience.

ETHENE.

OLEFIANT GAS.

Formula, C_2H_4. *Molecular Weight*, 27.8.

This gas is the first member of the second series of hydrocarbons, known as the *olefine series*, to which it has given the name.

Preparation.—The gas is best prepared by heating, in a capacious glass flask, a mixture of 1 part of alcohol with 6 parts of

sulphuric acid ; when the gas is evolving rapidly a further quantity of a mixture of 1 part alcohol and 2 parts acid is run slowly in, so as not to cool the contents of the flask sufficiently to retard the evolution of the gas. The reaction involved may be expressed as follows :

$$\underset{\text{Alcohol.}}{C_2H_6O} = \underset{\text{Ethene.}}{C_2H_4} + \underset{\text{Water.}}{H_2O.}$$

The sulphuric acid simply plays the part of a dehydrating agent, and brings about the reaction by its affinity for the water.

Properties.—Ethene, or ethylene, is a colorless gas, having a peculiar, suffocating, ethereal odor. Its specific gravity is 0.9688. At a temperature of 10.10° and a pressure of 51 atmospheres it liquefies, and boils at —103° under ordinary atmospheric pressure. It is soluble in 8 parts of water. Ethylene is an easily combustible gas, burning with a very luminous flame and evolving much smoke. It forms a mixture with 3 volumes of oxygen, which explodes violently on the application of flame. It forms an oily liquid with an equal volume of chlorine, which is known as the "oil of the Dutch chemists." From this the name of "olefiant gas" is derived.

ACETYLENE.

ETHINE.

Formula, C_2H_2. *Molecular Weight*, 25.8.

Preparation.—Acetylene may be prepared by the direct union of carbon and hydrogen. This is accomplished when the carbon electrodes of a powerful battery approach each other in an atmosphere of hydrogen. It also results whenever there is imperfect combustion of substances rich in carbon and hydrogen. When calcium carbide is brought into contact with water, acetylene is evolved according to the following reaction :

$$\underset{\text{Calcium Carbide.}}{CaC_2} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Acetylene.}}{C_2H_2} + \underset{\text{Calcium Hydrate.}}{Ca(OH)_2.}$$

Properties.—Acetylene is a colorless gas, with a peculiar, disagreeable odor. It is condensed to a liquid at 1° and under a pressure of 48 atmospheres. It is moderately soluble in water. Acetylene is combustible, burning with a bright but smoky flame. It is burned for illumination. See also page 618.

ILLUMINATING GAS.

COAL GAS.

History.—Gas was first used for illuminating purposes in the house of William Murdock, at Redruth, in Cornwall, England. He distilled coal in an iron retort, and lighted his house with the

gas which he thus manufactured. This occurred about 1792. Gas was used for lighting the streets of London in 1812, and those of Paris in 1815.

Preparation.—Illuminating gas is prepared by the destructive distillation of bituminous coal, although occasionally some other substances rich in carbon, like rosin, are used.

The process is accomplished in iron or fire-clay retorts, ten to twelve feet in length and two or three feet in diameter. Usually five of these retorts are placed in a furnace together. The temperature employed approaches low redness.

The products of this dry distillation are : (1) coke, (2) water, (3) tar, (4) ammonium carbonate, (5) liquid hydrocarbons, (6) hydrogen sulphide, (7) carbon dioxide, (8) carbon monoxide, (9) sulphur dioxide, (10) hydrogen, (11) marsh gas, (12) olefiant gas, and some other gaseous hydrocarbons.

Of these, 8, 10, 11, and 12 are useful for combustion and illumination ; 1 is valuable for fuel ; 3, 4, and 5 have other uses, to be considered later. The volatile products are first passed into the hydraulic main, where the water and tar are separated. From thence the gas goes into condensers, in which more tarry and oily liquids are removed. It then passes into the scrubbers, which consist of one or more columns of coke over which a spray of water trickles ; this serves to wash the gas and remove ammonia. Next come the purifiers, in which the gas comes in contact with dry calcium hydrate or ferric hydrate, which serves to remove the sulphur compounds and carbon dioxide. From the purifiers the gas goes into the gasometers for storage and distribution.

The average yield per ton of coal is from ten to twelve thousand cubic feet.

Coal gas is considerably lighter than air, its specific gravity varying from 0.65 to 0.75.

The value of gas for illuminating purposes is determined by comparing the light from a jet burning five feet per hour with the light from a sperm candle consuming one hundred and twenty grains per hour. Such a gas flame should be equal to thirteen or fourteen candles.

CARBON AND OXYGEN.

There are two well-known compounds of these two elements :

Carbon monoxide, CO.
Carbon dioxide, CO_2.

CARBON MONOXIDE.

Formula, CO. *Molecular Weight*, 27.78.

This compound is formed when coal burns with an incomplete supply of air. It may be easily recognized in the combustion of anthracite coal by its peculiar blue flame. Almost identical with this formation of it is the one by passing carbon dioxide over red-hot charcoal:

$$CO_2 + C = 2CO.$$

The carbon may be replaced by iron and the same result attained. Carbon monoxide is most easily prepared by heating oxalic acid and concentrated sulphuric acid together:

$$H_2C_2O_4 = CO_2 + CO + H_2O.$$

The sulphuric acid acts by its affinity for water, and so causes a breaking down of the oxalic acid molecule.

The mixed gases are passed through a strong solution of sodium hydrate to absorb the carbon dioxide.

In a similar manner formic acid, or a formate, may be decomposed by sulphuric acid; in this case, however, no carbon dioxide is formed:

$$HCHO_2 = CO + H_2O.$$

An economical method and one that will yield the gas rapidly consists in heating finely powdered potassium ferrocyanide with eight or ten times its weight of strong sulphuric acid:

$K_4Fe(CN)_6$	+	$6H_2SO_4$	+	$6H_2O$	=	$2K_2SO_4$	+	$3(NH_4)_2SO_4$	+
Potassium Ferrocyanide.		Sulphuric Acid.		Water.		Potassium Sulphate.		Ammonium Sulphate.	

$FeSO_4$	+	$6CO$.
Ferrous Sulphate.		Carbon Monoxide.

As soon as the reaction commences the heat must be removed and the vessel cooled, if necessary, in order to prevent too rapid evolution of the gas. The water necessary in the above reaction is derived from the water of crystallization in the potassium ferrocyanide and from the small quantity in the commercial sulphuric acid.

Properties.—Carbon monoxide is a colorless gas, with a peculiar odor. It is very slightly soluble in water and has no effect on litmus paper. It readily burns in air or oxygen with a peculiar pale-blue flame, the product of its combustion being carbon dioxide:

$$CO + O = CO_2.$$

When added to half its volume of oxygen, a mixture is formed which explodes on the application of flame.

The action of carbon monoxide on the human system is that of a narcotic poison. A small amount in the air is sufficient to produce giddiness and headache, followed by insensibility. Its peculiar action appears to be due to the formation of a compound with the hæmoglobin of the blood, the latter acquiring a purplish color.

CARBON DIOXIDE.

Formula, CO_2. *Molecular Weight*, 43.89.

History.—Carbon dioxide was discovered by Paracelsus about 1520, and was further investigated by Van Helmuth in the early part of the seventeenth century. Its chemical nature was first made out by Lavoisier.

Occurrence.—Carbon dioxide occurs free in the atmosphere to the extent of three or four volumes in ten thousand. It is found in many mineral waters, and in the craters of some extinct volcanoes. Combined with various bases as carbonates it is still more abundantly distributed. The principal one of these compounds is calcium carbonate, which, as marble, limestone, and chalk, is one of the most abundant of minerals.

Preparation.—Carbonates and bicarbonates when heated yield the gas according to the following:

$$CaCO_3 = CaO + CO_2.$$
$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

When small quantities are desired it is rapidly and conveniently made from marble and hydrochloric acid:

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

The same result may be attained by the use of sulphuric acid, but the calcium sulphate which is formed is quite insoluble, and therefore difficult to remove from the flask.

When a current of air is passed over red-hot carbon the product is carbon dioxide, provided the air be kept in excess. This and the method by heating a carbonate are used for furnishing the gas in the manufacture of carbonates on the large scale.

Properties.—Carbon dioxide is a colorless gas with a faint odor and weak acid taste. It is 1.52 times heavier than air and 21.945 times heavier than hydrogen. 1 volume of water dissolves 1 volume of the gas at ordinary atmospheric pressure. This solubility of the gas is increased 1 volume for every increase of 1 atmosphere in pressure.

A solution containing about 5 volumes of the gas in water constitutes the so-called "soda-water" which is dispensed in the pharmacies of this country. This solution is prepared by generating the gas from marble dust and sulphuric acid, in closed copper generators, and, after purifying the gas by passing it through water containing sodium bicarbonate, it is passed into water in steel cylinders, which are constantly agitated in order to facilitate the absorption. Only porcelain-lined steel cylinders and block-tin pipes should be used. Lead and copper are dissolved by the solution. It was formerly the custom to store the solution in copper cylinders lined with tin. In such vessels the soda-water frequently becomes contaminated with copper. The water should give no coloration with ammonium hydrate or sulphide, and no precipitate with potassium ferrocyanide, thus indicating the absence of copper.

The gas is more soluble in alcohol than in water.

Under a pressure of 35 atmospheres at a temperature of 0° carbon dioxide is condensed to a colorless, mobile liquid. This liquid has a specific gravity of 0.923 at 0°, and 0.782 at 20°. It is not miscible with water, and has no action on dry litmus paper. When liquid carbon dioxide is suddenly released from pressure, such an intense degree of cold is produced as to cause a portion of the liquid to solidify. This solidification may also be accomplished by cooling the liquid to —65°. This solid carbon dioxide is capable of producing an intense degree of cold; to accomplish this the solid is mixed with ether and placed under the receiver of an air pump. On account of the rapid vaporization of the oxide a temperature of —110° is produced. This solid may be handled with safety, as it is always surrounded by a thin layer of the gas; when, however, it is pressed into contact with the skin it will cause a blister.

Carbon dioxide is neither combustible nor a supporter of combustion. This property may be illustrated by lowering a lighted taper into a vessel of it, or, since it is heavier than air, by pouring it down an inclined board on which are placed a number of lighted candles. Under the name of "choke damp" it sometimes collects in old wells, and is detected by lowering a lighted candle, which will be extinguished if the gas is present. This choke damp results from the explosion of marsh gas in mines, and frequently fatally supplements the destruction caused by the latter.

When present in the atmosphere to the extent of 1 per cent.

inconvenience in breathing is experienced, and 10 per cent. will cause insensibility. Its deleterious action on respiration results from the exclusion of oxygen rather than from any inherent poisonous property of the gas. It may be taken into the stomach in aqueous solution with advantage in many cases.

Carbon dioxide when dissolved in water appears to form a definite compound, carbonic acid, as follows :

$$\underset{\text{Carbon Dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Carbonic Acid.}}{H_2CO_3}.$$

This solution reddens litmus paper, and is decomposed by heat, the gas escaping with effervescence.

Uses.—Carbon dioxide is employed in the manufacture of carbonates ; its solution in water is extensively used as a beverage ; and it forms an important constituent of the chemical fire extinguishers. Apart from these, and on a much larger scale, it assists in the growth of plant life. Large quantities of it are thrown into the atmosphere by man and animals ; it is there decomposed by the chlorophyll of plants aided by sunlight ; the carbon resulting from this decomposition goes to make up the structure of the plant, while the oxygen is rejected and returns to maintain the proper proportion of that element in the atmosphere.

Carbonates.—The salts of carbonic acid are usually prepared by passing carbon dioxide into a solution of a hydrate of the base :

$$2KOH + CO_2 = K_2CO_3 + H_2O,$$

or they are formed by double decomposition between a soluble carbonate and a soluble salt of the base :

$$\underset{\text{Sodium Carbonate.}}{5Na_2CO_3} + \underset{\text{Magnesium Sulphate.}}{5MgSO_4} + \underset{\text{Water.}}{6H_2O} = \underset{\text{Magnesium Carbonate.}}{(MgCO_3)_4,Mg(OH)_2.5H_2O} + \underset{\text{Sodium Sulphate.}}{5Na_2SO_4} + \underset{\text{Carbon Dioxide.}}{CO_2}.$$

The carbonates of the alkalies are soluble in water, all others are insoluble. The carbonates of the alkalies, alkaline earths, and some metals are quite stable ; the acid carbonates are decomposed on heating and by boiling their aqueous solutions.

Percarbonates.—When a saturated solution of potassium carbonate is electrolyzed at a low temperature, the disengagement of oxygen at the anode ceases at —10° C. Instead of the formation of bicarbonate, the result is a bluish amorphous powder, potassium percarbonate, $K_2C_2O_6$. It oxidizes many substances, but may act as a reducing agent.

PRACTICAL EXERCISES.

(1) Place a few pieces of marble (calcium carbonate) in a flask arranged as for the preparation of hydrogen, cover with water, and add hydrochloric acid; a brisk evolution of carbon dioxide occurs. The gas may be collected over water, although it is somewhat soluble in that liquid; it may also be collected by downward displacement, as it is considerably heavier than air.

(2) Pour some clear lime water into a jar of the gas and agitate; the solution immediately becomes cloudy, owing to the formation of insoluble calcium carbonate. If the gas be passed in for some time the liquid will become nearly clear again, on account of the solubility of the precipitate in excess of carbonic acid.

(3) Add solution of potassium hydrate to a test-tube or jar of the gas, close, and agitate well; the gas is absorbed by the alkali, as may be shown by placing the vessel under water and removing the stopper, when the water will rush in, nearly filling it.

(4) A lighted taper lowered into the gas is immediately extinguished. The same result is accomplished by pouring the gas into the vessel some distance above the flame and allowing the gas to settle down upon it. The latter experiment also illustrates the weight of the gas, which is twenty-two times heavier than hydrogen.

COMBUSTION AND ILLUMINATION.

1. Chemical Nature of Combustion.—This is in all ordinary cases a combination of the burning body with oxygen, supplied by the air, which is the usual supporter of combustion. This is readily established by examining the products of combustion, which in these cases are oxides. They may be solids as with the products of the combustion of metals, liquids as in the case of hydrogen oxide, or water, or gases as in the case of the oxides of carbon.

As these combustions involve direct chemical union of the elements concerned, it matters not which is the combustible body and which the supporter of combustion. We may in many cases easily reverse the ordinary conditions. Thus, a jet of hydrogen or illuminating gas will burn in an atmosphere of air or oxygen because the hydrogen or the hydrocarbons of the illuminating gas combine chemically with the oxygen. For the same reason, a jet of oxygen will burn in an atmosphere of hydrogen or illuminating gas if such be arranged. A jet of air will also burn in the atmosphere of illuminating gas, the air being for the time called the combustible body and the illuminating gas the supporter of combustion.

2. Conditions of Combustion.—Combustion may be slow or rapid, accompanied by flame or not, according to conditions.

The appearance of flame indicates a burning gas, which may be given off even when solids or liquids are taken, in consequence of the heat. A certain temperature is necessary for flame. The temperature of a gaseous combustion may be so lowered that the flame is extinguished. For instance, metallic gauze has this effect upon a flame because of its excellent conducting powers whereby the temperature is rapidly lowered. If a piece of gauze is pressed down upon a lighted gas-jet the flame will not penetrate the gauze, or if the gas be lighted above the gauze the flame will not communicate to the gas issuing below. The Davy safety-lamp is an application of this principle.

3. The Structure of Flame.—An ordinary candle flame or gas-jet, as shown in Fig. 111, is composed of several cones. The inner cone contains gaseous hydrocarbons not as yet ignited, the middle cone contains an excess of carbon rendered incandescent at the temperature of the flame, while the outer cone is bluish and has no unconsumed carbon.

FIG. 111.

Candle flame.

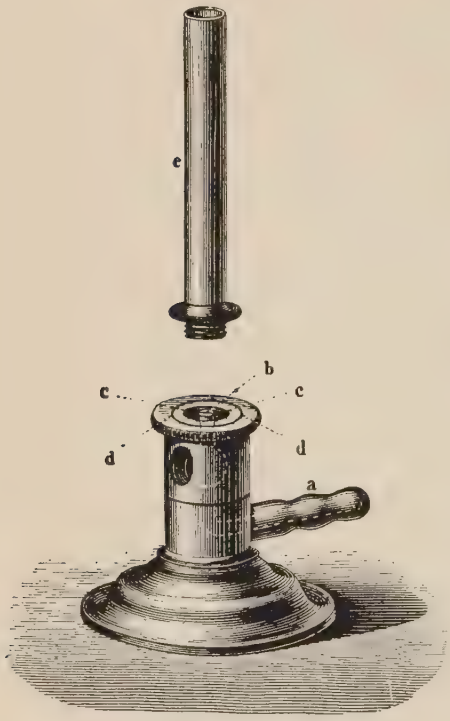
The fact that unconsumed hydrocarbon gases exist in the inner cone of a gas flame can be demonstrated by introducing a small glass tube obliquely from one side and taking off this gas to be burned. A phosphorus match may also be held with the head placed in this point of no combustion, and the phosphorus composition will melt but not ignite until withdrawn and allowed to come in contact with the air.

4. Distinction between Luminous and Non-Luminous Flames.—While, as stated, the appearance of flame indicates a burning gas, the luminosity of the flame depends upon the separation in the flame of small solid particles rendered incandescent by the heat. Thus, in the ordinary gas flame we have particles of carbon separated and rendered incandescent. If sufficient oxygen or air be admitted to the cone of the flame, the hydrocarbon gases will be consumed without separation of carbon. This may be done in either one of two ways, —by the aid of the blowpipe or blast lamp, which directs a current of air directly into the cone of the flame, or by mixing air with the illuminating gas before it is burned, as in the Bunsen burner.

The mouth blowpipe is often used for the purpose of directing a small but very hot flame upon any object. We are capable of

getting two quite distinct chemical effects by its aid. If the long pointed blowpipe flame be examined it will be seen that we have an inner and an outer blue cone. If the substance to be heated be placed just within the bounds of the inner cone, we get a reducing effect; that is, it is deoxidized, because of the deficiency of oxygen here; if, on the other hand, the substance be heated by the outer cone of the flame, we get an oxidizing effect, because of the excess of oxygen present in this part of the flame.

FIG. 112.



Bunsen burner.

The Bunsen burner, as shown in Fig. 112, is a most convenient form of apparatus for changing a luminous flame into a non-luminous one. As seen in the illustration, the gas first issues from a small jet. Here it would tend to burn with the yellow luminous flame. But a tall chimney is screwed on to an outer casing surrounding the jet and air is admitted through openings in the base of this chimney. The gas issuing from the inner jet produces a strong upward draft in the chimney, and a mixture of gas and air therefore rises and is ignited at the top of the chimney.

Two methods of changing the non-luminous flame into a luminous flame exist. We may pass a gas like hydrogen over volatile hydrocarbons, like benzene, petroleum-ether, or naphthalene, and so enrich it with hydrocarbon vapors, or we may direct a hot non-luminous flame like that of the oxyhydrogen blowpipe upon solids like caustic lime, which are thereby rendered incandescent. Both methods are of practical application, as in the carburetting of water-gas and in the production of the "lime-light."

CARBON AND SULPHUR.

CARBON DISULPHIDE.

Formula, CS_2. *Molecular Weight*, 75.56.

Carbon disulphide was discovered by Lampadius in 1796. It is prepared by a direct union of the elements at a red heat. For this purpose a cast-iron cylinder or earthenware retort is filled with charcoal, and heated to redness; sulphur is then introduced at the bottom; the vapor rising combines with the carbon and passes over into a series of condensers. Some hydrogen sulphide is formed at the same time, which is removed by agitation with mercury. The carbon disulphide is then redistilled. Fat or wax is sometimes added to the liquid before redistillation in order to assist in the removal of the more offensive-smelling compounds of sulphur.

Properties. — Carbon disulphide is a colorless, mobile, strongly-refracting liquid, which, as it comes in commerce, usually has a fetid odor, due to various sulphur impurities, but when purified as above described, is of a mild ethereal odor. It is insoluble in one thousand parts of water, but mixes in all proportions with absolute alcohol, ether, chloroform, and the fixed and volatile oils. It solidifies at —116° and melts at —113°. Its vapor is very inflammable, taking fire in the air at 149°; this may be effected by bringing a test tube of paraffin heated to this temperature in contact with it. The result of its combustion is carbon dioxide and sulphur dioxide:

$$CS_2 + 3O_2 = CO_2 + 2SO_2.$$

The vapor when mixed with nitrogen dioxide readily burns, on the application of flame, with a peculiar bluish flame, which is very rich in actinic rays. The vapor acts as a poison on man and animals, even in very small amount; if it be inhaled for some time it will produce serious effects upon the nervous system.

Uses.—Carbon disulphide is used extensively in the arts on account of its great solvent action on oils and rubber. It has been extensively used in France to destroy the grape pest or *phylloxera*. For the latter purpose it is often first converted into a sulphocarbonate of sodium. (See also *Xanthogenates* under Organic Chemistry.)

Detection.—Carbon disulphide is detected by mixing a small

quantity of the liquid with alcoholic ammonia, and evaporating on a water-bath, when ammonium sulphocyanate is formed :

$$\underset{\text{Carbon Disulphide.}}{CS_2} + \underset{\text{Ammonia.}}{4NH_3} = \underset{\text{Ammonium Sulphocyanate.}}{NH_4SCN} + \underset{\text{Ammonium Sulphide.}}{(NH_4)_2S}.$$

On acidifying the residue with hydrochloric acid, and adding ferric chloride solution, the red color of ferric sulphocyanate is developed.

Sulphocarbonic or Thiocarbonic Acid, H_2CS_3.—When sodium hydrate is brought in contact with carbon disulphide, the sodium salt of thiocarbonic acid is formed :

$$\underset{\text{Sodium Hydrate.}}{6NaOH} + \underset{\text{Carbon Disulphide.}}{3CS_2} = \underset{\text{Sodium Thiocarbonate.}}{2Na_2CS_3} + \underset{\text{Sodium Carbonate.}}{Na_2CO_3} + \underset{\text{Water.}}{3H_2O}.$$

The free acid is obtained when hydrochloric acid is added to ammonium thiocarbonate :

$$(NH_4)_2CS_3 + 2HCl = 2NH_4Cl + H_2CS_3.$$

This acid is a yellowish-brown, heavy oil, which easily decomposes, when heated, into hydrogen sulphide and carbon disulphide :

$$H_2CS_3 = H_2S + CS_2.$$

The thiocarbonates of the alkalies and alkaline earths are soluble in water. The potassium salt mixed with carbonate is obtained when carbon disulphide is added to potassium hydrate solution, and is used as a remedy against *phylloxera*. Its action depends on the carbon disulphide which is liberated when the mixture comes in contact with earth.

Carbonyl Sulphide, COS, is supposed to exist in some sulphur waters. It may be obtained by the direct union of carbon monoxide and sulphur vapor, when passed through a red-hot tube ; but it is more easily made by acting on potassium sulphocyanate with sulphuric acid :

$$\underset{\text{Potassium Sulphocyanate.}}{KCNS} + \underset{\text{Sulphuric Acid.}}{2H_2SO_4} + \underset{\text{Water.}}{H_2O} = \underset{\text{Acid Ammonium Sulphate.}}{NH_4HSO_4} + \underset{\text{Acid Potassium Sulphate.}}{KHSO_4} + \underset{\text{Carbonyl Sulphide.}}{COS}.$$

It is a colorless gas, with a disagreeable, sulphuretted odor ; very inflammable, burning with a bright blue flame. It is soluble in an equal volume of water, and this solution gradually decomposes into carbon dioxide and hydrogen sulphide :

$$COS + H_2O = CO_2 + H_2S.$$

CHAPTER VIII.

CLASSIFICATION OF THE ELEMENTS.

PERIODIC SYSTEM.

REFERENCE has been made in a previous section to a comprehensive classification of the elements. While this has hitherto been based on valence in the main, it can now be made to cover much more and to indicate many additional points of relationship between the elements.

As early as 1817 it was pointed out that certain elements possess striking similarities in their chemical and physical properties. In 1829 Doebereiner classified these, arranging them into groups or families of three, pointing out their chemical, physical, and mathematical relationship. Arranged in accordance with this triadic theory, we have, for example :

	Atomic Weight.	Difference.		Atomic Weight.	Difference.
K	39		Cl	35.4	
		46			44.6
Rb	85		Br	80	
		48			46.5
Cs	133		I	126.5	
Ca	40		Mg	24	
		47			41
Sr	87		Zn	65	
		50			47
Ba	137		Cd	112	

It will be observed that the atomic weight of the middle element of each group is nearly the arithmetical mean of the two extremes ; the differences in the last column are almost the same in the case of each group.

In 1865 Newlands proposed his law of octaves, in which he, after arranging the elements in order of their increasing atomic weights, found that after each series of seven elements the first one of the following series presents analogies to the same numbered one of the preceding. Thus, the elements Li, Na, K, Rb, and Cs are closely related, as well as F, Cl, Br, and I (see table below).

In 1869 Mendelejeff and Lothar Meyer independently elaborated these views, and developed what is known as the *periodic law of the elements*,—namely, *the properties of the elements* (*and their compounds*) *are periodic functions of the atomic weights.* Quoting from Lothar Meyer : "If the elements are arranged in the order of increasing atomic weights, the properties of these

elements vary from member to member of the series, but return more or less nearly to the same value at certain fixed points in the series." This will be made evident in the explanations of the following table :

							* 1. Li	Be	B	C	N	O	F.			
							7	9	11	12	14	16	19			
							2. Na	Mg	Al	Si	P	S	Cl.			
							23	24	27	28	31	32	35.4			
3.	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni		Cu	Zn	Ga	Ge	As	Se	Br.
	39	40	44	48	51	52	55	56	59	58.7		63.5	65	70	72	75	79	80
4.	Rb	Sr	Yt	Zr	Nb	Mo	—	Ru	Rh	Pd		Ag	Cd	In	Sn	Sb	Te	I.
	85	87	89	91	94	96	100	102	103	106		108	112	114	119	120	126	126.5
5.	Cs	Ba	La	Ce	Di	—	Sa	—	—	—		—	—	—	—	—	—	—
	133	137	138	140	142		150											
6.	—	—	Yb	—	Ta	W	—	Os	Ir	Pt		Au	Hg	Tl	Pb	Bi	—	—
			173		183	184		191	193	195		197	200	204	207	208		
7.	—	—	—	Th	—	Ur	—	—	—	—		—	—	—	—	—	—	—
				232		240												

It will be observed that Periods 1 and 2 consist of seven members, while the remainder are arranged in periods of seventeen (7 + 3 + 7). The elements at the beginning and the end of both large and small periods show almost complete analogy in physical and chemical properties. Thus, K, Rb, and Cs resemble Li and Na ; Ca, Sr, and Ba resemble Be and Mg ; also Zn and Cd agree with Be and Mg. As we approach the middle members of these periods the similarity disappears gradually, only to reappear again towards the end of the periods. Thus, I and Br resemble Cl and F ; Te and Se resemble S and O ; Sb and As resemble P and N. These semblances gradually disappear, reappearing again towards the other ends, as has already been shown.

Further analogies which exist between the various members of these periods may be illustrated in Period 2 :

	Na	Mg	Al	Si	P	S	Cl.
a. Valency, hydrogen	I	II	III	IV	III	II	I.
b. Valency, oxygen	I	II	III	IV	V	VI	VII.
c. Specific gravity	0.97	1.75	2.67	2.5	2	1.9	1.3 (liquid).
d. Atomic volume†	24	14	10	11	14	16	27.
e. Hydroxides . .	$NaOH$	$Mg(OH)_2$	$Al(OH)_3$	$Si(OH)_4$	$P(OH)_5$	$S(OH)_6$	$Cl(OH)_7$.

* In the tables of the Periodic System the atomic weights are rounded off to whole numbers wherever possible, those based on O = 16 being given the preference on this account.

† The atomic volume (specific volume) of an element is the quotient obtained by dividing its atomic weight by its specific gravity. It expresses the relative volumes of the atoms.

In all periods there is a gradual and regular change in the chemical and physical properties, showing a maximum or minimum value at either extremity or middle of the period. Thus, the hydrogen valencies (*a*) and specific gravities (*c*) form two curves, which unite in the middle, forming a maximum. On the other hand, the oxygen valencies (*b*) and hydroxides (*e*) form a curve which rises gradually from its minimum at Na to a maximum at Cl. The atomic volumes (*d*) form two curves, with two maximums at the extremities and one minimum in the middle.

Selecting Periods 1 and 2, if we add 16 to the atomic weight of each element in Period 1, we will obtain a figure close in value to the atomic weight of the one immediately below it in Period 2. These elements also exhibit similar chemical properties. For example, Li $7 + 16 = 23$, which is that of Na (23); Be $9 + 16 = 25$, Mg is 24; C $12 + 16 = 28$, Si is 28; F $19 + 16 = 35$, Cl is 35.4.

Where in the small periods (1 and 2) the maximum valency of the oxides increases gradually towards the extremity, we find that in the large periods (3, 4, 5) this increases with a double periodicity. Thus,—

I	II	III	IV	V	VI	VII
K_2O	CaO	Sc_2O_3	TiO_2	V_2O_5	CrO_3	Mn_2O_7.
		VI	IV	II		
		Fe_2O_3	CoO_2	NiO.		
I	II	III	IV	V	VI	VII
Cu_2O	ZnO	Ga_2O_3	——	As_2O_5	SeO_3	Br_2O_7.

As a result of this, the first and last seven members of these greater periods are arranged in two series and placed under the corresponding seven members of the smaller periods (see table, p. 346). This leaves the three middle members (Fe, Co, Ni, etc.) to be placed following the others, forming Group VIII.

Upon consulting the periodic table (see p. 346), it will be observed that the elements are not only divided into *periods* of 7 or $7 + 3$ members, but are also classified into *groups*, consisting of first and second sub-groups, the members of which exhibit special characteristics in common.

Thus, in Group I. all the metals of the first sub-group—that is, those on the left side of the column—are monads and strongly electro-positive. These elements form extremely basic compounds with oxygen, after the type M_2O or MX, and arranged in order of their increasing chemical energy they are Li, Na, K, Rb,

THE PERIODIC SYSTEM OF THE ELEMENTS (MENDELEJEFF).

	Series.	Group I.	Group II.	Group III.	Group IV.	Group V.	Group VI.	Group VII.	Group VIII.		
Hydrogen or Halogen Types		MX	MX_2	MX_3	MX_4	MX_3	MX_2	MX			
Highest Oxides		M_2O	MO	M_2O_3	MO_2	M_2O_5	MO_3	M_2O_7	MO_3	MO_2	MO
Period 1	1	H 1									
	2	Li 7	Be 9	B 11	C 12	N 14	O 16	F 19			
Period 2	3	Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35.4			
Period 3	4	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56	Co 59	Ni 58.7
	5	Cu 63	Zn 65	Ga 70	Ge 72	As 75	Se 79	Br 80			
Period 4	6	Rb 85	Sr 87	Yt 89	Zr 90	Nb 94	Mo 96	— 100	Ru 101	Rh 103	Pd 106
	7	Ag 108	Cd 112	In 114	Sn 119	Sb 120	Te 127	I 126.5			
Period 5	8	Cs 133	Ba 137	La 138	Ce 140	Di 142	—	Sa 150	—	—	—
	9	—	—	—	Er 166	—	—	—			
	10	—	—	Yb 173	—	Ta 183	W 184	—	Os 191	Ir 193	Pt 195
	11	Au 197	Hg 200	Tl 204	Pb 207	Bi 208	—	—			
Period 6	12	—	—	—	Th 232	—	Ur 240	—			

and Cs. This is known as the *alkali* group, and presents many marked similarities in the physical and chemical characters of its members. In Group II., which is made up of dyads of the type MO or MX_2, Be and Mg belong to the small periods, and show some similarities, while Ca, Sr, and Ba, members of the three great periods, constitute the group of the *alkali earths*, which are less electro-positive than the alkalies of Group I. The triadic metals of Group III., which yield derivatives of the types M_2O_3 or MX_3, contain as first sub-group B, Al, Sc, Yt, La, and Yb, all of which resemble aluminum closely, and as a group possess but weak basic characters.

The tetrads C, Si, Ge, Sn, and Pb form a sub-group under Group IV., and from their slight electro-negative characters, as well as their central position between Groups I. and VII., they serve as a turning point from the electro-positive groups preceding, which gradually diminish in their positive characters from left to right, and the electro-negative groups following, which, increasing in their negative characteristics, culminate in the acid-forming metalloid group (VII.) consisting of F, Cl, Br, and I. The sub-groups (V.) consisting of N, P, As, Sb, and (VI.) comprising O, S, Se, Te, as well as the halogen (VII.) group, all form volatile compounds with hydrogen. Likewise similar volatile derivatives are obtained with various organic radicals, as $Si(CH_3)_4$, $P(CH_3)_3$, $S(CH_3)_2$, $ClCH_3$, etc.

The metals in the second sub-group of Group I.—namely, Cu, Ag, and Au—are monivalent, and form compounds isomorphous to those of the sodium sub-group. They exhibit among themselves great similarities physically and chemically; as, for example, the insolubility of their oxides and sulphides, also their chlorides (CuCl, AgCl, and AuCl) are insoluble in water and soluble in ammonia and thiosulphates, etc. Zn, Cd, and Hg, the second sub-group of Group II., present the same relationship to Mg as those under Group I. to Na, while among themselves many analogues may be found. The heavy metals, Ga, In, and Tl, of the second sub-group of Group III., are less basic than the aluminum sub-group, and bear a close relationship to one another.

The metals under Group VIII. exhibit many analogies which justify the formation of this group. For example, these elements are all of a gray color, and fuse at very high temperatures (Os = 2500° C., Ir = 1950° C., Fe = 1500° C.). Among them we find compounds of the type MO_4 (OsO_4, RuO_4, $Ni(CO)_4$,

$Fe(CO)_4$), indicating a general valence of VIII. They all form stable crystalline double salts with potassium cyanide, and occlude gases in a greater or less degree.

In the space afforded it is impossible to present more than an outline of the details of this periodic grouping of the elements. However, by means of this systematic gradation in the properties of the elements we are able not only to exert a control over the numbers of the atomic weights, but also the properties and atomic weights of undiscovered elements may be predicted with accuracy.

In general, the value of any property of an element is the mean between the values of the same property of the elements on all four sides of it in the table. When this table was first prepared there were gaps between boron and yttrium, between aluminum and indium, and between silicon and tin. To these hypothetical elements Mendelejeff assigned the names of eka-boron, eka-aluminum, and eka-silicon, and minutely described their properties. In 1875, 1879, and 1886 gallium, scandium, and germanium were discovered respectively with the properties assigned by Mendelejeff.

Professor Ramsay, in his endeavors to find a place in the periodic table for the newly discovered (1895) element argon, was led to the belief that this element constituted a member of a new period. With this in view, he instituted a search for other possible elements which, like argon, might be associated with nitrogen in the atmospheric air. This resulted in the discovery of helium, neon, krypton, and xenon.

The only explanation of the agreement in the properties of the elements with the atomic weights is that all the elements are aggregations of the same primordial substance. Hydrogen was once believed to be this substance, chiefly because of the fact that it looked at first as if the atomic weights of all the elements were simple multiples of the hydrogen atom. This has been shown to be incorrect by recent accurate atomic weight determinations. (See Prout's law.)

PART III.

CHEMISTRY OF THE METALS.

CHAPTER I.

THE ALKALI METALS.

General Characters.—The alkali group of metals consists of **Potassium, Sodium, Lithium, Rubidium, Cæsium,** and the atomic group **Ammonium.**

In this group, the valence of the individual members is the immediate reason for so classifying them. They have numerous other properties in common, for instance, their soft, wax-like consistence, their low specific gravity, all but rubidium and cæsium being lighter than water, their strong metallic lustre, and their low melting points. Of course, where the metals are to be compared, ammonium is excluded; but the compounds of all the members bear a close resemblance to one another. The metals all energetically decompose water, evolving hydrogen, and forming hydrates in solution which have a strongly alkaline reaction.

The salts are nearly all soluble in water, the chief exceptions being lithium phosphate and carbonate. Potassium, ammonium, rubidium, and cæsium form insoluble tartrates and chloroplatinates, while sodium and lithium do not. Some other distinguishing characters of their salts will be noted when they come to be treated analytically.

POTASSIUM.

Symbol, K. *Atomic Weight*, 39.03. *Valence*, I.

History.—The salts of potassium have been known from the earliest times. They were probably first extracted from wood ashes under the name *alkali*. Previous to 1736 there was no distinction between the salts of potassium and sodium. The former then became known as *potashes*.

The metal potassium was discovered in 1807 by Davy, who separated it by the electrolysis of potassium hydrate. Its elementary character was not finally admitted until 1811, after the investigations of Gay-Lussac and Thénard.

Occurrence.—Potassium is widely distributed in nature, but never in the metallic state. In the mineral kingdom it is found as nitrate or nitre, as the double magnesium and potassium chloride, or carnallite, and as the chloride, or sylvite. It occurs, however, most extensively as silicate in many rocks; especially in potash-feldspar, where it is found to the extent of 10 to 15 per cent. As feldspar is a constituent of granite, it will be seen that the distribution is very wide.

The other abundant rocks that contain potassium are syenite, gneiss, and micaceous schist. Many mineral waters, and the waters of the ocean, contain small proportions of the potassium salts.

Potassium is found abundantly in the vegetable and animal kingdoms. It is a necessary constituent of plants, and is absorbed by them from the soil. The condition in which it exists in the soil is usually as a compound with some organic acid. Plants obtain their supply of this element from the soil where it is stored. The soil retains more potassium than it does sodium. The animal body contains a considerable proportion of potassium salts. The salts of sodium are eliminated from the system while those of potassium are retained.

Sheep's wool contains nearly one-third its weight of potassium salts, which are known in commerce as *suint*.

Sources.—The world's supply of potassium salts is derived chiefly from the chloride and carbonate. The chloride of potassium is obtained from the carnallite and sylvite of Stassfurt, Germany. The output of chloride in 1891 was over 65,000 tons. A considerable quantity of the sulphate of potassium occurs at Stassfurt, with the chloride.

The carbonate is obtained from wood ashes, and the supply at the present time is chiefly furnished by Russia, although a distinct amount is produced in the United States and Canada. Small quantities of the carbonate are also obtained from the beet-root residues after the preparation of the sugar. The washings from sheep's wool, after evaporation and calcination, form an additional source for potassium salts in the form of carbonate.

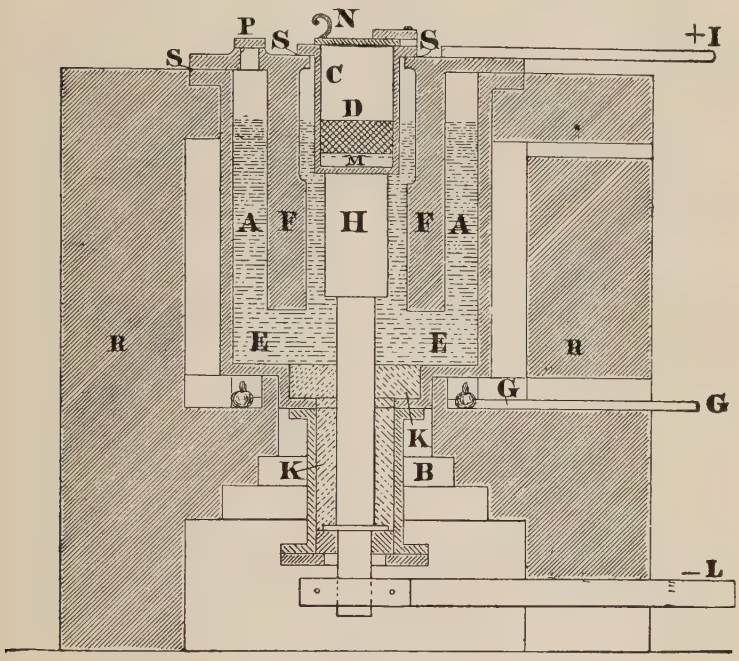
Preparation.—Potassium may be prepared by subjecting solid potassium hydrate to a strong electric current. The metal and

hydrogen are liberated at the negative pole and oxygen at the positive pole, as follows :

$$2KOH = K_2 + H_2 + O_2.$$

This process has been perfected by Castner, so as to render it available for producing the metal on a large scale. The apparatus by which this is accomplished is illustrated in Fig. 113.

FIG. 113.



Electrolytic preparation of potassium.

The iron vessel A contains the melted potassium hydrate, which is maintained in a fused condition by the gas-jets G. The negative electrode H is brought from the bottom, the positive electrode F is suspended from the top, and the two are separated by an iron wire cage. H is sealed in position by the metallic hydrate K below the gas-jets after it has cooled. The vessel and its attachments are supported by the brickwork R ; P is an aperture for the insertion of a thermometer, since it is important that the temperature of the hydrate be not allowed to rise more than twenty degrees above its fusing point.

When the decomposition takes place, the liberated potassium

rises and floats on the surface of the fused hydrate in c. It is removed by a finely-perforated spoon, which retains the metal and allows the melted hydrate to run through. The process is a continuous one, as more of the hydrate is added from time to time to replace that which is decomposed.

Potassium may also be prepared by heating to whiteness a mixture of potassium hydrate and metallic iron :

$$\underset{\text{Potassium Hydrate.}}{4KOH} + \underset{\text{Iron.}}{3Fe} = \underset{\text{Ferroso-ferric Oxide.}}{Fe_3O_4} + \underset{\text{Potassium.}}{2K_2} + \underset{\text{Hydrogen.}}{2H_2}.$$

The older method for the preparation of the metal on a large scale is that in which an intimate mixture of potassium carbonate and carbon is heated to whiteness. This mixture is best prepared by the ignition of acid potassium tartrate in closed crucibles, when the following decomposition occurs :

$$\underset{\text{Potassium Bitartrate.}}{2KHC_4H_4O_6} = \underset{\text{Potassium Carbonate.}}{K_2CO_3} + \underset{\text{Water.}}{5H_2O} + \underset{\text{Carbon Monoxide.}}{4CO} + \underset{\text{Carbon.}}{3C}.$$

The residue of potassium carbonate and carbon is mixed with a little more charcoal, and brought to a strong white heat in a furnace similar to that shown in Fig. 115, and used in the preparation of sodium. The reaction which takes place is as follows :

$$\underset{\text{Potassium Carbonate.}}{K_2CO_3} + \underset{\text{Carbon.}}{C_2} = \underset{\text{Potassium.}}{K_2} + \underset{\text{Carbon Monoxide.}}{3CO}.$$

The retort consists of a wrought-iron mercury flask covered with fire-clay to prevent oxidation. It is adapted to a flat receiver in order to facilitate rapid cooling and prevent the formation of a black compound of potassium and carbon monoxide. The liquid potassium as it condenses is allowed to run into petroleum, in order to preserve it from oxidation. This process was brought into practical operation by Brunner, but has since been improved upon by others, and very extensively employed. It is likely, however, to be superseded by the electrolytic method. The potassium prepared in this manner is still in need of purification by redistillation, as it is liable to be contaminated with carbon monoxide, which, unless removed, may give rise to the black explosive compound.

A method was devised by Castner, previously to his electrolytic one, in which it was proposed to furnish the metal at an expense not exceeding twenty-five cents a pound. This consists in first obtaining an iron carbide, FeC_2, an intimate mixture of fine

iron and coke. This is then heated with potassium hydrate to about 800°, when the following reaction takes place :

$$\underset{\text{Potassium Hydrate.}}{6KOH} + \underset{\text{Iron Carbide.}}{FeC_2} = \underset{\text{Potassium Carbonate.}}{2K_2CO_3} + \underset{\text{Hydrogen.}}{3H_2} + \underset{\text{Iron.}}{Fe} + \underset{\text{Potassium.}}{K_2}.$$

The potassium carbonate is reconverted into hydrate and used again.

Properties.—On account of the rapidity with which potassium combines with oxygen, it is found in commerce chiefly in the form of small globular pieces of the size of cherries, and preserved under petroleum or other hydrocarbon, to protect it from the air.

Potassium is of a waxy consistence, and when freshly cut exhibits the true appearance of the metal, which is silver white in color and of a bright metallic lustre. Next to lithium, it is the lightest metal known, having a specific gravity of 0.865. On the application of heat it melts at 62.5°, and at a low red heat, in an atmosphere of some inert gas like hydrogen or nitrogen, it volatilizes, yielding a greenish vapor.

By melting some of the metal in a tube surrounded by nitrogen gas, allowing to cool until a portion solidifies, and pouring out the liquid portion, that remaining in the tube takes the form of tetragonal octohedra, of a silver-white color.

Potassium dissolves in liquid ammonia, forming a deep blue solution, and, as the liquid evaporates, it is left unchanged.

Potassium has a strong affinity for oxygen, and its vapor bursts into flame on coming in contact with air, burning with a characteristic violet color. If air be absolutely free from moisture, it will not combine with the metal at ordinary temperatures. When thrown on water, the latter is immediately decomposed, the metal combining with the oxygen and liberating the hydrogen, which with some potassium vapor bursts into a violet-colored flame.

Potassium combines with the halogens with great energy ; a small fragment dropped on bromine causes a violent explosion. It has the power to displace most other metals from their combinations, and has, therefore, been used for preparing magnesium and aluminum.

POTASSIUM AND HYDROGEN.

Potassium Hydride, K_4H_2.—When potassium is heated in an atmosphere of hydrogen to 300° a silver-white, brittle mass results, which begins to decompose at 410°, or, under reduced pressure, dissociation begins at 200°. Potassium hydride inflames spontaneously on contact with air.

POTASSIUM AND THE HALOGENS.

The halogen compounds of potassium are:

Potassium fluoride, KF.
Potassium chloride, KCl.
Potassium bromide, KBr.
Potassium iodide, KI.

Potassium Fluoride, KF, is prepared by neutralizing aqueous hydrofluoric acid, in a platinum dish, with potassium carbonate or hydrate. On concentrating the solution the salt crystallizes out in cubes. When formed at ordinary temperatures these crystals have the formula $KF.2H_2O$, but at or above 35° they form without water of crystallization.

The salt is deliquescent, and its solution attacks glass. Hydrofluoric acid has the property of forming acid salts; of these, the one with potassium, KHF_2, is characteristic. The other halogens appear not to have this property of forming acid salts.

Potassium Chloride, KCl.—This salt was first used in medicine by Sylvius de le Boë, under the name of *sal febrifugum* or *sal digestivum*. It occurs in sea water, in many mineral springs, and at Stassfurt, Germany. As carnallite, $KCl\,MgCl_2.6H_2O$, and sylvite, KCl, it is the most abundant salt in that locality.

Preparation.—Since potassium chloride occurs so abundantly in nature, it is rarely prepared on the small scale. It can, however, readily be made by neutralizing hydrochloric acid with potassium carbonate, according to the following reaction:

$$\underset{\text{Potassium Carbonate.}}{K_2CO_3} + \underset{\text{Hydrochloric Acid.}}{2HCl} = \underset{\text{Potassium Chloride.}}{2KCl} + \underset{\text{Carbon Dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O}.$$

On the large scale carnallite is mixed with three-fourths its weight of water, and the mixture treated for some time with live steam, whereby the carnallite is resolved into its constituent salts, magnesium chloride and potassium chloride. The hot solution is allowed to cool, and the less soluble potassium chloride crystallizes. It is further purified by washing with a little cold water and recrystallizing.

Properties.—Potassium chloride occurs in permanent, white, cubical crystals; soluble in 3 parts of cold water, in about 2 parts of hot water, and insoluble in alcohol. Its specific gravity at 15° is 1.945. On the application of strong heat the salt melts, and at a red heat it volatilizes.

Uses.—Potassium chloride is used for the preparation of a number of other potassium salts, notably the chlorate and carbonate. The impure salt is used largely as a fertilizer.

Potassium Bromide, KBr. **Potassii Bromidum, U. S. P.**—This salt is prepared by one of two methods:

(1) 1 part of iron wire in a large flask is covered with 10 parts of water; 2 parts of bromine are slowly added, in small portions at a time, allowing the combination with the iron to take place after each addition. This part of the operation should be conducted in a well-ventilated room, in order that the operator may avoid inhaling the irritating fumes that are unavoidably evolved. In the reaction which takes place ferrous bromide is formed, as follows:

$$Fe + Br_2 = FeBr_2.$$

The resulting solution is of a green color, and is then filtered from the excess of iron. It is then heated in an open dish to near the boiling point, and 1.75 parts of potassium carbonate in 10 parts of water are slowly added until, after heating a short time, the liquid reacts slightly alkaline. The result is a mixture of potassium bromide and ferrous carbonate:

$$\underset{\text{Ferrous Bromide.}}{FeBr_2} + \underset{\text{Potassium Carbonate.}}{K_2CO_3} = \underset{\text{Potassium Bromide.}}{2KBr} + \underset{\text{Ferrous Carbonate.}}{FeCO_3}.$$

The mixture is heated for some time in order to convert the bulky precipitate of ferrous carbonate into a more compact ferrous and ferric hydrate, carbon dioxide escaping at the same time. The whole is then filtered and the precipitate washed free of potassium bromide by means of hot water. The clear filtrate, containing the potassium bromide, is evaporated and crystallized.

(2) To a convenient quantity of potassium hydrate solution bromine is added in small portions at a time, until, after agitation, the yellow-brown color of the bromine remains permanent, indicating a slight excess of that element. The following reaction expresses what has taken place:

$$\underset{\text{Potassium Hydrate.}}{6KOH} + \underset{\text{Bromine.}}{3Br_2} = \underset{\text{Potassium Bromide.}}{5KBr} + \underset{\text{Potassium Bromate.}}{KBrO_3} + \underset{\text{Water.}}{3H_2O}.$$

The solution is evaporated nearly to dryness, and a quantity of wood charcoal stirred in amounting to one-tenth of the amount of bromine. The mixture is then dried and heated to low redness in an iron vessel, when the reduction of the potassium bromate is accomplished as follows:

$$KBrO_3 + 3C = KBr + 3CO.$$

The cooled mass is treated with water, the solution filtered and evaporated to crystallization.

Properties.—When perfectly pure, potassium bromide occurs in colorless, translucent, cubical crystals, permanent in the air, odorless, with a sharp saline taste and a neutral reaction. The commercial salt usually occurs in white, opaque crystals with a slightly alkaline reaction. The salt is soluble in 1.6 parts of water at 15°, and in less than one part of boiling water. It is soluble in 200 parts of cold and in 16 parts of boiling alcohol; also soluble in 4 parts of glycerin. When heated the salt decrepitates somewhat, and at 700° it fuses without decomposition. At a bright red heat it volatilizes, imparting to the flame a violet color.

Potassium bromide is identified by the usual potassium tests and by adding to 10 c.c. in a test-tube a few drops of chloroform and then, a little at a time, chlorine water until the solution smells distinctly of it; a yellowish-brown color is imparted to the chloroform on agitation. If a violet color be produced iodide is indicated. An admixture of potassium bromate is indicated when an immediate yellow color is assumed on the addition of diluted sulphuric acid. This test depends on the following reaction:

$$5KBr + KBrO_3 + 6H_2SO_4 = 6KHSO_4 + 3H_2O + 3Br_2.$$

Potassium Iodide, KI. **Potassii Iodidum, U. S. P.**—This salt is prepared by mixing in a capacious porcelain dish 1 part of iron wire with 8 parts of water, and adding in small portions at a time 3 parts of iodine. The result is ferrous iodide, as follows:

$$Fe + I_2 = FeI_2.$$

The greenish solution is filtered from the undissolved iron, and treated with 1 part of iodine, forming ferric iodide:

$$2FeI_2 + I_2 = Fe_2I_6.$$

To this solution are added 2.2 parts of pure potassium carbonate, previously dissolved in 10 parts of water. The following reaction takes place:

Fe_2I_6	+	$3K_2CO_3$	+	$3H_2O$	=	$6KI$	+	$3CO_2$	+	$Fe_2(OH)_6$.
Ferric Iodide.		Potassium Carbonate.		Water.		Potassium Iodide.		Carbon Dioxide.		Ferric Hydrate.

If necessary a small additional quantity of potassium carbonate may be added until the solution is faintly alkaline. The whole mixture is then boiled for a few minutes, which causes the precipitate to become more dense; it is then filtered and washed. The filtrate and washings are concentrated to a small bulk and set aside for the potassium iodide to crystallize out.

Another method consists in adding to a convenient quantity of potassium solution sufficient powdered iodine in small portions at a time to produce a permanent yellowish color. Potassium iodide and iodate are formed as follows :

$$\underset{\text{Potassium Hydrate.}}{6KOH} + \underset{\text{Iodine.}}{3I_2} = \underset{\text{Potassium Iodide.}}{5KI} + \underset{\text{Potassium Iodate.}}{KIO_3} + \underset{\text{Water.}}{3H_2O.}$$

The solution is evaporated to a syrupy consistence, and a quantity of wood charcoal, equal to one-tenth the amount of iodine employed, is stirred in. The mixture is then dried and heated to low redness. The iodide is unchanged by this treatment, while the iodate is converted into iodide according to the following reaction :

$$KIO_3 + 3C = KI + 3CO.$$

The residue, after cooling, is treated with water, filtered, and the filtrate, after concentration, is set aside to crystallize.

Finally, potassium iodide is prepared from the "mother liquors" obtained in the preparation of sodium nitrate from Chili saltpetre, iodine being recovered as cuprous iodide, Cu_2I_2. This is converted into hydrogen iodide as follows :

$$Cu_2I_2 + H_2S = Cu_2S + 2HI.$$

The hydrogen iodide, after removal of cuprous sulphide by filtration, is neutralized with potassium carbonate.

Properties.—Potassium iodide is ordinarily found in large, white, opaque crystals, having been crystallized from a faintly alkaline solution. When the crystals are formed in neutral solutions, they are colorless and nearly transparent. The salt has a faint odor, and a sharp, saline taste with a faint, bitterish aftertaste. The crystals are permanent in dry air, but slightly deliquescent in moist air.

The salt is soluble in 0.75 part water at 15°, and in 0.5 part of boiling water, in 18 parts alcohol, and in 6 parts boiling alcohol ; it is also soluble in 2.5 parts of glycerin.

When heated the salt decrepitates, and at a low red heat it fuses ; at a bright red heat it volatilizes without decomposition. The aqueous solution should have a scarcely perceptible alkaline reaction towards litmus paper. The salt becomes of a faint yellowish color when exposed to the air, on account of the liberation of traces of iodine.

The usual tests for potassium serve to identify the salt as containing that base, and the iodine is indicated by adding a few

drops of chloroform to the aqueous solution, and then chlorine water in small portions at a time until the solution smells of it, when, on agitation, a violet color will be imparted to the chloroform ; iodine is also liberated from this salt by fuming nitric acid, by concentrated sulphuric acid, and by chromic acid. Silver nitrate produces a yellow precipitate of silver iodide when added to a solution of potassium iodide. This precipitate is insoluble in nitric acid and in ammonium hydrate.

Uses.—Potassium iodide is used largely in medicine.

Potassium Tri-iodide, KI_3.—When a concentrated solution of potassium iodide is saturated with iodine, a dark-brown liquid is formed, which, when evaporated at ordinary temperatures over sulphuric acid, yields nearly black, acicular crystals, possessing a metallic lustre. These crystals are very deliquescent, melt at 45°, and at 100° decompose into potassium iodide and iodine. The solution of these crystals is a useful reagent for alkaloids. It usually gives brown precipitates, soluble in alcohol.

POTASSIUM AND OXYGEN.

There are two well-defined potassium oxides :

Potassium monoxide, K_2O.
Potassium peroxide, K_2O_2.

At least one other oxide, having the formula K_4O, is supposed to exist, but it has never been prepared pure, and when formed readily changes to the monoxide.

Potassium Oxide, K_2O, is obtained, together with some peroxide, by heating the metal in dry air. When this mixture is strongly heated it evolves oxygen and the monoxide remains. It is also prepared by heating the metal with potassium hydrate :

$$2KOH + K_2 = 2K_2O + H_2.$$

The oxide, when pure, is a white powder or brittle mass ; it fuses at a high temperature and volatilizes somewhat. Its affinity for water is so intense that when moistened with that liquid it becomes red-hot. Potassium hydrate is the result of this combination with water.

Potassium Peroxide, K_2O_2, is obtained when the metal is heated with an excess of oxygen. It is a yellow mass which gives up oxygen when heated to whiteness. On treatment with water, it dissolves, with the formation of potassium hydrate, hydrogen peroxide, and oxygen.

The blue compound which is formed when potassium is burned with an insufficient amount of air is the suboxide, K_4O.

Potassium Hydrate, KOH. **Potassa,** U. S. P.—This compound, which is also known as potassium hydroxide and caustic potash, appears to have been first observed by Geber in the eighth

century, and was considered to be an element until Davy demonstrated its compound nature in 1807.

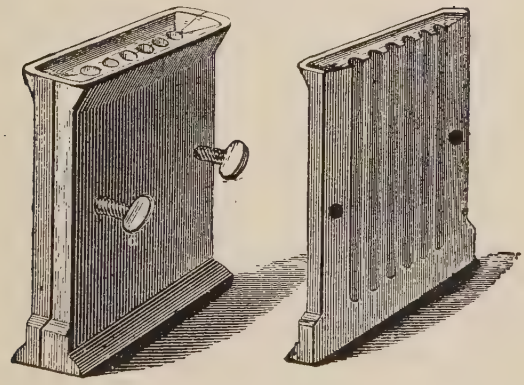
Preparation.—Potassium hydrate is prepared by slaking 3 parts of calcium oxide with a small quantity of water, and then rubbing to a fine powder with 10 parts of water. This is added in small portions at a time to 4 parts of potassium carbonate, previously dissolved in 15 to 20 parts of water. The mixture is then heated to the boiling point for twenty minutes, the heat removed, and the vessel closely covered until the liquid has settled clear. Water must be added from time to time during the heating, for if the solution become too concentrated a reverse reaction sets in. The operation is known to be complete when a portion of the clear solution gives no effervescence on supersaturating with an acid. The reaction which takes place in the formation of the hydrate is as follows :

K_2CO_3	+	$Ca(OH)_2$	=	$2KOH$	+	$CaCO_3$.
Potassium Carbonate.		Calcium Hydrate.		Potassium Hydrate.		Calcium Carbonate.

The clear liquid is removed from the sediment by a siphon, and evaporated in an iron dish to a specific gravity of 1.16, when it begins to attack the iron, and further concentration must be conducted in a silver vessel.

When the liquid has assumed an oily consistence, and a drop removed on a glass rod solidifies on cooling, it is poured into silver moulds. The moulds are illustrated in Fig. 114. Potassium

FIG. 114.



Moulds for potassium hydrate.

hydrate is also obtained as one of the products in the electrolytic production of chlorine. (See page 196.) In order to obtain a

product free from aluminum hydrate, sulphates, and chlorides, 1 part of the potassium hydrate is dissolved in from 3 to 4 parts of highly rectified alcohol, the clear liquid decanted from the sediment, boiled down in a silver dish, and cast in moulds as before. A still purer potassium hydrate is sometimes prepared by dissolving metallic potassium in water.

Properties.—Potassium hydrate, when pure, is a white, crystalline, brittle solid. It is odorless, and has a sharp, caustic taste, and an alkaline reaction. It is soluble in 0.5 part of water at 15°, and in 2 parts of alcohol; it is very soluble in boiling water and in boiling alcohol. When heated to a temperature of 530°, it melts to a clear oily liquid, and at a bright red heat it is volatilized unchanged. It absorbs carbon dioxide and water from the air, and dissolves in the latter with evolution of heat. When the concentrated aqueous solution is cooled, a compound containing two molecules of water, $KOH.2H_2O$, crystallizes out in tabular or octohedral crystals. The solution in alcohol rapidly assumes a dark-yellow to brown color, and in the presence of air there are formed acetic acid, aldehyde, and aldehyde resin.

The **Liquor Potassæ** of the Pharmacopœia contains about 5 per cent. of the hydrate, and has a specific gravity of about 1.036. The official process directs that this solution be made from potassium bicarbonate and lime, since the bicarbonate is found purer in commerce than the normal carbonate.

The commercial caustic potash usually contains from 75 to 90 per cent. of absolute potassium hydrate, and 10 to 25 per cent. of water.

OXYGEN SALTS OF POTASSIUM AND THE HALOGENS

Potassium Hypochlorite, KClO, is known only in solution. It is the active ingredient in "Eau de Javelle," which is prepared by passing chlorine into cold dilute solution of potassium carbonate or hydrate. The result is a solution of potassium hypochlorite and chloride. This solution was formerly much used for bleaching purposes.

Potassium Chlorate, $KClO_3$. **Potassii Chloras**, U. S. P.—This salt was discovered and first prepared by Berthollet in 1786.

Preparation.—The simplest method of preparing potassium chlorate on a small scale is by passing chlorine into a strong, hot solution of potassium hydrate:

$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O.$$

Owing to the formation at the same time of a considerable

quantity of potassium chloride, this is rather an expensive process, and on a commercial scale other methods have been introduced.

The commercial production of potassium chlorate is accomplished by treating milk of lime with an excess of chlorine in a vessel in which the mixture is constantly agitated. The result is calcium chlorate and chloride, as follows :

$$\underset{\text{Calcium Hydrate.}}{6Ca(OH)_2} + \underset{\text{Chlorine.}}{6Cl_2} = \underset{\text{Calcium Chloride.}}{5CaCl_2} + \underset{\text{Calcium Chlorate.}}{Ca(ClO_3)_2} + \underset{\text{Water.}}{6H_2O}.$$

After allowing the mixture to settle, the clear liquid is drawn off and evaporated with potassium chloride to a specific gravity of 1.28, when the following reaction takes place between the calcium chlorate and the potassium chloride :

$$Ca(ClO_3)_2 + 2KCl = 2KClO_3 + CaCl_2.$$

The potassium chlorate, being rather insoluble in water, crystallizes out, and, after separation, it is purified by dissolving in hot water and recrystallizing.

It has been proposed to use magnesium oxide suspended in water instead of milk of lime, on account of the resulting magnesium chloride having less solvent action on the potassium chlorate than is possessed by the calcium chloride.

Another commercial process consists in mixing solutions of potassium chloride and calcium hypochlorite (bleaching powder). The whole is then cooled, when potassium chlorate separates out :

$$\underset{\text{Potassium Chloride.}}{2KCl} + \underset{\text{Calcium Hypochlorite.}}{3(Ca(OCl)_2 + CaCl_2)} = \underset{\text{Potassium Chlorate.}}{2KClO_3} + \underset{\text{Calcium Chloride.}}{6CaCl_2}.$$

Potassium chlorate is also prepared by electrolysis. When anodes and cathodes are placed opposite each other in a solution of potassium chloride, but without being separated by a porous diaphragm, the electric current gives rise to the formation of potassium hypochlorite. If the solution of this compound be boiled, potassium chlorate is obtained :

$$\underset{\text{Potassium Hypochlorite.}}{3KClO} = \underset{\text{Potassium Chlorate.}}{KClO_3} + \underset{\text{Potassium Chloride.}}{2KCl}.$$

Properties.—Potassium chlorate occurs in "colorless, lustrous, monoclinic prisms or plates, or a white powder, odorless, and having a cooling, saline taste. Permanent in the air. Soluble in 16.7 parts of water at 15°, and in 1.7 parts of boiling water ; insoluble in absolute alcohol, and but slightly soluble in mixtures of alcohol and water."

When heated to 334° the salt melts, and at 352° it commences to decompose into oxygen, potassium chloride, and perchlorate. At about 400° the perchlorate is decomposed, with further evolution of oxygen, potassium chloride only remaining.

Uses.—One of the principal uses of potassium chlorate is in the preparation of oxygen on a small scale. It is also largely employed as an oxidizing agent in calico-printing. In the manufacture of colored fires this salt plays an important part. It has considerable use in medicine, especially in diseases of the throat.

Potassium chlorate should never be ground or rubbed with organic substances or with sulphur, as violent explosions are almost sure to occur. In case it is necessary to make such mixtures, the ingredients should be powdered separately, and then carefully mixed without friction.

Mixtures of potassium chlorate and ammonium chloride have exploded violently after standing for some time.

Colored fires are made by taking 25 to 50 parts of potassium chlorate and 25 parts of powdered sugar or shellac as a base ; to this mixture are added 25 parts of strontium nitrate for red, 25 parts of barium nitrate for green, 10 parts of copper nitrate for blue, and 10 parts of sodium nitrate or chloride for yellow. Sulphur may be used in place of sugar or shellac, but the resulting powder is more liable to decompose with combustion or explosion.

Potassium Perchlorate, $KClO_4$, is prepared by heating potassium chlorate to 352°, when it is decomposed into perchlorate, chloride, and oxygen ; the oxygen escapes, and the two salts remain behind as a pasty mass.

This is cooled, powdered, and treated with cold water, which removes the potassium chloride. The undissolved residue is digested with warm hydrochloric acid to decompose chlorate and convert it into chloride, which is then washed out with cold water. The residue consists of nearly pure perchlorate.

The perchlorate is one of the most insoluble of potassium salts, requiring 65 parts of cold and 5.04 parts of boiling water to dissolve it. It is practically insoluble in alcohol.

Potassium Bromate, $KBrO_3$.—When bromine is added to potassium hydrate, the following reaction takes place :

$$6KOH + 3Br_2 = KBrO_3 + 5KBr + 3H_2O.$$

It may be more economical to pass chlorine into a hot solution of potassium bromide and hydrate, as follows :

$$KBr + 6KOH + 3Cl_2 = KBrO_3 + 6KCl + 3H_2O.$$

The bromate crystallizes out on concentrating and cooling.

Another convenient method of preparation is to decompose barium bromate with potassium sulphate; the mixture is heated to the boiling point, the insoluble barium sulphate is removed by filtration from the solution of potassium bromate, and the latter allowed to cool and crystallize. The salt occurs in six-sided plates or prisms, and is quite insoluble in cold water.

Potassium Iodate, KIO_3.—When chlorine is passed into cold water holding iodine in suspension, until the latter disappears, iodine monochloride, ICl, is formed; to this is added the molecular proportion of potassium chlorate and the mixture warmed, when chlorine is evolved and potassium iodate separates out in cubical crystals:

$$ICl + KClO_3 = KIO_3 + Cl_2.$$

The salt is soluble in 13 parts of cold water, and decomposes, when strongly heated, into potassium iodide and oxygen.

Potassium Periodate, KIO_4, is prepared by passing chlorine into a mixture of potassium iodate and hydrate. The salt separates out in small rhombic crystals, and requires 300 parts of cold water for solution. Between 250° and 300° it decomposes into potassium iodate and oxygen, and at a higher temperature it parts with all of its oxygen, leaving a residue of potassium iodide.

POTASSIUM AND SULPHUR.

Potassium monosulphide, K_2S. Potassium tetrasulphide, K_2S_4.
Potassium disulphide, K_2S_2. Potassium pentasulphide, K_2S_5.
Potassium trisulphide, K_2S_3. Potassium hydrosulphide, KSH.

Potassium Monosulphide, K_2S, is prepared by heating to redness in a well-covered vessel an intimate mixture of 7 parts of potassium sulphate and 2 parts of finely-powdered charcoal, when the following reaction takes place:

$$K_2SO_4 + 4C = K_2S + 4CO.$$

The same compound is obtained when one volume of potassium hydrate solution is saturated with hydrogen sulphide, and then mixed with an equal volume of the same strength potassium hydrate solution:

$$KOH + H_2S = KSH + H_2O.$$
$$KSH + KOH = K_2S + H_2O.$$

Properties.—When potassium monosulphide is treated with a small proportion of water, it dissolves unchanged, and will crystallize from its solution with 5 molecules of water. When, however, it is treated with a larger quantity of water, it decomposes into the hydrosulphide and hydrate, as follows:

$$K_2S + H_2O = KSH + KOH.$$

On the application of heat it melts to a black liquid, which cools to a reddish, crystalline mass.

Potassium Hydrosulphide, KSH, is formed when hydrogen sulphide is passed into a solution of potassium hydrate; by evaporating this solution in a vacuum, crystals are formed containing 1½ molecules of water.

The remaining potassium sulphides may be appropriately termed polysulphides, and may be formed by heating the monosulphide with the molecular proportion of sulphur, observing at the same time the proper degree of heat.

Potassa Sulphurata, U. S. P., is a mixture of polysulphides with potassium sulphate and thiosulphate. It is prepared by fusing together sulphur and potassium carbonate.

"When freshly prepared, sulphurated potassa forms irregular pieces of a liver-brown color, which, by exposure to the air, gradually absorb moisture, oxygen, and carbon dioxide, and change to a greenish-yellow, and finally to a gray mass containing potassium carbonate, hyposulphite, and sulphate.

"Soluble in 2 parts of water at 15°, with the exception of a small residue. Alcohol dissolves only the potassium sulphide, leaving the other constituents (hyposulphite and sulphate) undissolved."

OXYGEN SALTS OF POTASSIUM AND SULPHUR.

Potassium Sulphite, $K_2SO_3.2H_2O$.—The salt of this formula is the normal potassium sulphite. It is prepared by passing sulphur dioxide into a solution of potassium carbonate, until the mixture reacts strongly acid:

$$K_2CO_3 + 2SO_2 + H_2O = 2KHSO_3 + CO_2.$$

To this solution potassium carbonate is added to a neutral or faintly alkaline reaction. The slight excess of sulphur dioxide forms the acid sulphite, which, on the addition of the carbonate, is converted into neutral or normal sulphite, as follows:

$$2KHSO_3 + K_2CO_3 = 2K_2SO_3 + CO_2 + H_2O.$$

The solution is concentrated without much heat, and monoclinic octohedral crystals separate out.

Potassium sulphite is somewhat deliquescent, odorless, and has a bitter, saline, sulphurous taste. It has a neutral or feebly alkaline reaction. It is more soluble in cold than in hot water, requiring 4 parts of water at 15° and 5 parts of boiling water for solution, alcohol has very slight solvent action. On the application of heat, the salt loses its water of crystallization, amounting to 18.5 per cent. At a higher temperature, decomposition takes place, with the formation of potassium sulphate, sulphite, and hydrate, the residue, therefore, has an alkaline reaction.

Acid Potassium Sulphite, $KHSO_3$, is prepared from potassium carbonate and sulphur dioxide, according to the equation given under the

normal sulphite. It forms in monoclinic prisms, but by adding alcohol to the concentrated aqueous solution, it may be obtained in acicular crystals. The salt is very soluble in water, has a neutral or slightly alkaline reaction, and emits the odor of sulphur dioxide. On exposure to air it gradually changes to sulphate.

Potassium Disulphite, or Pyrosulphite, $K_2S_2O_5$, is formed when sulphur dioxide is passed into a hot saturated solution of potassium carbonate until effervescence ceases and the liquid assumes a greenish tinge. On cooling, the salt separates in granular crystals. It is difficultly soluble in water, and has an acid, disagreeable taste.

Potassium Sulphate, K_2SO_4. **Potassii Sulphas, U. S. P.**—This salt has been known since the fourteenth century. It occurs in many mineral waters, in sea water, and in the ashes of many plants. The chief locality of its occurrence is in the Stassfurt salt-beds. Kainite is a double sulphate of potassium and magnesium with magnesium chloride, $K_2SO_4MgSO_4MgCl_2.5H_2O$; schoenite is a double sulphate of potassium and magnesium, $K_2SO_4 2MgSO_4.6H_2O$.

These two minerals form the chief sources of the salt. It may be obtained as a by-product in the manufacture of nitric acid from potassium nitrate and sulphuric acid, in the manufacture of potassium bichromate, in the decomposition of potassium tartrate by calcium sulphate, in the manufacture of sulphuric acid, and in the manufacture of potassium carbonate from potassium chloride in the Leblanc process.

Preparation.—In the preparation of the salt from kainite, the mineral is exposed to the air until the more soluble magnesium chloride deliquesces and runs off. The remaining salt is dissolved in boiling water, which decomposes it, and, on cooling, the less soluble potassium sulphate crystallizes first.

Properties.—Potassium sulphate occurs in "hard, colorless, transparent, six-sided, rhombic prisms terminated by pyramids, or a white powder, odorless, and having a somewhat bitter, saline taste. Permanent in the air. Soluble in about 9.5 parts of water at 15°, and in 4 parts of boiling water; insoluble in alcohol. When heated, the crystals decrepitate. At a bright red heat they fuse, and at a white heat the salt suffers partial decomposition. The aqueous solution is neutral to litmus paper." The specific gravity of the crystals is 2.648.

Potassium sulphate has some uses in medicine, and it is extensively employed in the preparation of potash alum and potassium carbonate.

Acid Potassium Sulphate (Potassium Bisulphate), $KHSO_4$.—This salt is found native in the Grotto del Sofo, near Naples, in the form of long acicular crystals. Its usual source and method of preparation are from the residue of the manufacture of nitric acid from potassium nitrate when an excess of sulphuric acid has been used.

When the salt is separated from an acid solution, it is obtained in the form of tabular rhombic crystals, which are easily soluble in water. From dilute solutions of the acid sulphate the neutral sulphate crystallizes; following this, as the solution is concentrated, there separates a salt having the composition $K_2SO_4KHSO_4$, and then the acid salt crystallizes. From this it appears that in dilute solution the acid salt is dissociated into neutral potassium sulphate and sulphuric acid. This is also observed when the acid salt is mixed with alcohol: a decomposition takes place, the neutral sulphate separates, while the sulphuric acid passes into solution in the alcohol.

Acid potassium sulphate fuses at 200°, and above that temperature is converted into *potassium pyrosulphate*, $K_2S_2O_7$. This salt at a temperature of 600° decomposes into neutral sulphate and sulphur trioxide.

Potassium pyrosulphate crystallizes in long needles, and when brought in contact with water evolves much heat and is converted into the acid sulphate.

Acid Potassium Disulphate, KHS_2O_7, is formed when the pyrosulphate is dissolved in fuming sulphuric acid, and from this liquid it is deposited in transparent prismatic crystals.

Acid potassium sulphate is useful as a flux, because in this way it is possible to bring sulphuric acid in contact with many bodies at a temperature considerably above its boiling point.

OXYGEN SALTS OF POTASSIUM AND NITROGEN.

Potassium Nitrate (Saltpetre, Nitre), KNO_3. **Potassii Nitras, U. S. P.**—Saltpetre was known in the eighth century. It is very widely distributed in nature, mixed more or less with other salts, chiefly calcium nitrate. It is found most abundantly in the warm climates of India, Egypt, Hungary, and South America. Formerly most of the salt came from India. It is made there by collecting the efflorescence from stables and other places where nitrogenous matter is undergoing decomposition with free access of air. This efflorescence is obtained from large heaps of manure, on which urine is poured daily. As the surface dries and shows the presence of the salt, it is removed, and this process repeated until the bed, after two or three years, become exhausted. The crude liquors are treated with potassium carbonate, which precipitates the calcium, and the clear liquid is separated and concentrated to crystallize.

The greatest production of the salt now is from Chili saltpetre,

sodium nitrate, by double decomposition with potassium chloride, as follows :

$NaNO_3$	+	KCl	=	KNO_3	+	NaCl.
Sodium Nitrate.		Potassium Chloride.		Potassium Nitrate.		Sodium Chloride.

The hot saturated solutions of these two salts are mixed and concentrated until the solution reaches a specific gravity of 1.5, when the sodium chloride, being no more soluble in hot than in cold water, separates out and is removed. The liquid is then drawn off and allowed to cool, when the potassium nitrate crystallizes in fine powder. This is removed and washed with a small quantity of cold water, which removes the last of the sodium chloride. The salt is then purified by recrystallization.

In order more fully to explain this method of preparing the salt, the following solubilities are given :

	15°.	100°.
100 parts of water dissolve KNO_3 .	26 parts.	247 parts.
100 parts of water dissolve $NaNO_3$.	86.3 "	168.2 "
100 parts of water dissolve KCl . .	33.4 "	56.6 "
100 parts of water dissolve NaCl .	36 "	39.2 "

Properties.—Potassium nitrate occurs in "colorless, transparent, six-sided, rhombic prisms, or a crystalline powder, odorless, and having a cooling, saline, and pungent taste. Permanent in the air. Soluble in 3.8 parts of water at 15°, and in 0.4 part of boiling water; very sparingly soluble in alcohol. When heated to 353°, the salt melts. At a higher temperature it is decomposed, giving off oxygen at first, and then some of its nitrogen, leaving a residue of potassium nitrate, nitrite, and oxide. Thrown on red-hot coals, the salt deflagrates. The aqueous solution is neutral to litmus paper."

Uses.—Potassium nitrate is used in medicine and as a preservative ; in the latter capacity it enters into the composition of most of the meat preservatives, boric acid, borax, and sodium carbonate being the other compounds usually associated with it. The chief use of potassium nitrate is in the manufacture of gunpowder. The average composition of gunpowder is as follows :

Potassium nitrate	74.9 parts.
Charcoal	13.3 "
Sulphur	11.8 "
	100.00 "

In actual practice the composition varies somewhat from the above, since charcoal is not a uniform substance, consequently the character of the charcoal used in each case must be taken into account. The amount of the constituents is also varied according to the purposes to which the powder is to be applied.

Potassium Nitrite, KNO_2.—This salt is usually prepared by fusing in an iron vessel 1 part of potassium nitrate, to which are then added, in small portions at a time, 2 parts of powdered metallic lead; the latter is rapidly oxidized, as follows:

$$KNO_3 + Pb = KNO_2 + PbO.$$

On cooling, the mass is treated with water, and from the solution of the potassium nitrite any lead is removed by carbon dioxide. The solution is then concentrated to a small bulk and the undecomposed nitrate allowed to crystallize out. The clear solution of now nearly pure nitrite is next evaporated to dryness, which yields the salt in masses of small, indistinct crystals. It is deliquescent in moist air, but nearly insoluble in alcohol. It usually comes in commerce in sticks of a yellowish color.

OXYGEN SALTS OF POTASSIUM AND PHOSPHORUS.

There are three potassium salts of orthophosphoric acid.

Tripotassium Orthophosphate, K_3PO_4, is prepared by heating to redness phosphoric acid and potassium carbonate or hydrate. It is readily soluble in water, and separates in small, colorless, acicular crystals.

Dipotassium Orthophosphate, K_2HPO_4.—This salt is formed when orthophosphoric acid is neutralized with potassium carbonate. The resulting compound is difficult to crystallize.

Monopotassium Orthophosphate, KH_2PO_4, is produced when the above dipotassium compound is heated with an excess of orthophosphoric acid. It usually separates in large, colorless, rhombic crystals.

There are two potassium salts of pyrophosphoric acid, according as two or four atoms of hydrogen are replaced by the base.

Potassium Pyrophosphate, $K_4P_2O_7$, is obtained by neutralizing pyrophosphoric acid with potassium hydrate, or, perhaps, more conveniently by heating the dipotassium orthophosphate to redness. It is a deliquescent salt which separates from solution in fibrous crystals, containing three molecules of water.

Dipotassium Pyrophosphate, $K_2H_2P_2O_7$.—This is the acid salt, and is prepared by dissolving the neutral salt in acetic acid and precipitating with alcohol.

Potassium Metaphosphate, KPO_3, is prepared by heating the monopotassium orthophosphate to redness. As thus obtained it is in translucent masses, nearly insoluble in water, but readily soluble in dilute acids. Although monobasic, metaphosphoric acid possesses the property of polymerization, so that there are at least five compounds of potassium with the acid, having the following formulas: KPO_3, metaphosphate; $K_2P_2O_6$, dimetaphosphate; $K_3P_3O_9$, trimetaphosphate, etc.

Potassium Hypophosphite, KH_2PO_2. **Potassii Hypophosphis**, U. S. P.—This salt is prepared by decomposing calcium hypophosphite with potassium carbonate, as follows:

$$\underset{\text{Calcium Hypophosphite.}}{Ca(H_2PO_2)_2} + \underset{\text{Potassium Carbonate.}}{K_2CO_3} = \underset{\text{Potassium Hypophosphite.}}{2KH_2PO_2} + \underset{\text{Calcium Carbonate.}}{CaCO_3}.$$

The details of the process are to add 5.75 parts of potassium carbonate, in 8 parts of water, to 6 parts of calcium hypophosphite, in 64 parts of water; allow to stand until the precipitate settles, filter, and evaporate the filtrate at a temperature not exceeding 100° until granulation is effected. By failing to keep below the temperature specified an explosion is liable to occur. The product is purified by dissolving in alcohol, evaporating to a syrupy consistence, and crystallizing.

Potassium hypophosphite occurs in "white, opaque, hexagonal plates, or crystalline masses, or a granular powder, odorless, and having a pungent, saline taste; very deliquescent. Soluble, at 15°, in 0.6 part of water, and in 7.3 parts of alcohol; in 0.3 part of boiling water, and in 3.6 parts of boiling alcohol; insoluble in ether. When heated in a dry test-tube, the salt at first loses moisture, and then evolves spontaneously inflammable hydrogen phosphide gas, which burns with a bright yellow flame."

This salt should not be rubbed with nitrates, chlorates, permanganates, or other oxidizing agents, as, under these circumstances, it will explode violently.

OXYGEN SALTS OF POTASSIUM AND BORON.

Potassium Metaborate, KBO_2, is formed when molecular weights of boric oxide and potassium carbonate are fused together. The product is soluble in water and crystallizes with difficulty.

There are several other borates, the most important of which is the tetraborate, $K_2B_4O_7.5H_2O$. It is prepared by adding potassium hydrate to a solution of boric acid until an alkaline reaction is obtained. This compound resembles the corresponding sodium salt, which will be treated more fully.

OXYGEN SALTS OF POTASSIUM AND SILICON.

Potassium Silicate, K_2SiO_3, is produced when amorphous silica or silicic acid is dissolved in potassium hydrate. It is also formed when silica is fused with potassium carbonate. It occurs in amorphous vitreous masses, which readily deliquesce when exposed to the air and gradually become converted into a transparent jelly, which then shrinks to a hard mass.

Potassium Tetrasilicate, $K_2Si_4O_9$.—This is the soluble potash glass. It is prepared by fusing together 45 parts of quartz with 30 parts of potas-

sium carbonate and 3 parts of charcoal. The fused mass is dissolved in 5 times its weight of boiling water and concentrated to the desired strength.

Potassium Fluosilicate, K_2SiF_6, is prepared by precipitating any salt of potassium with hydrofluosilicic acid. The resulting compound is quite insoluble in cold water, but readily dissolves in that solvent when hot

OXYGEN SALTS OF POTASSIUM AND CARBON.

Potassium Carbonate, K_2CO_3.—The more or less pure carbonates of potassium are known as *potash*, *pearlash*, and *salt of tartar*, according to their degree of purity.

Source.—The chief sources of potassium carbonate are: (1) Wood-ashes, (2) beet-root molasses, (3) sheep's wool, and (4) potassium chloride and sulphate.

(1) Wood-ashes. All land plants contain potassium salts, and these, when the plants are burned, are almost entirely converted into carbonate. Russia, America, and Hungary, on account of their plentiful supply of timber, furnish most of the carbonate from this source.

The following are some of the percentages of potassium yielded by different woods:

Pine	0.045	Oak	0.153
Poplar	0.075	Willow	0.285
Beech	0.145	Elm	0.390

In America much lye (a solution of potassium carbonate and hydrate) is made in a small way by those who use wood for fuel. The apparatus in which this is accomplished consists of a square wooden hopper or percolator of two or three hundred pounds capacity, in the bottom of which is placed a layer of straw, then a layer of quick-lime, and then alternate layers of ashes and quick-lime to the top, the last layer being a thick one of ashes. Water is poured on in small quantities at a time for a week or so, and the resulting solution, which is collected underneath, consisting of potassium carbonate and hydrate, is used for the manufacture of soft soap.

On the large scale the lixiviation is carried out the same as that described above, except that the use of lime appears to be confined to America. Wood is usually the material employed for procuring the carbonate, although in Eastern Russia grass, the green portions of potatoes, and other vegetables are burned for their ash.

For commercial purposes the solution resulting from the lixivi-

ation of the ashes is evaporated to dryness in iron pans, and the dark-brown product contains from 6 to 12 per cent. of water. The color, which is due to organic matter, is removed by heating the salt to about 800° ; the mass at first blackens, but slowly becomes white, when the heat is removed, the salt cooled, and packed immediately in air-tight casks.

Russian potash is said to contain from 50 to 60 per cent. of potassium carbonate and some hydrate. The American product is usually purified by solution in water, re-evaporated and ignited, when it contains from 75 to 90 per cent. of absolute carbonate ; it is then known as pearlash. Most of the potash in the market contains more or less sulphate, sometimes as much as 18 per cent. During the concentration of the lye liquor the sulphate crystallizes out. Formerly this was raked out and used in the manufacture of alum.

The American potash is chiefly produced in Canada. In 1892, 1,409,200 pounds passed under observation of the government at Montreal. Birch and maple are the chief wood there consumed in this industry.

(2) When the molasses from beet-root sugar is allowed to ferment, and is then distilled, there remains a residue which contains 30 to 35 per cent. of potassium carbonate, 18 to 20 per cent. sodium carbonate, and smaller amounts of chlorides, sulphates, and insoluble matter ; this residue is calcined, dissolved in a small quantity of water, and the clear solution again evaporated and calcined, whereby the percentage of potassium carbonate is increased to an amount that warrants its use as pearlash.

(3) Sheep's wool contains a relatively large amount of potassium combined with some inorganic acids, but chiefly with the stearic, oleic, palmitic, and benzoic acids.

When the wool is washed these compounds go into solution, and, on evaporation and ignition, the residue is found to contain about 30 per cent. of potassium carbonate. The processes of solution, evaporation, and ignition are repeated, whereby the percentage of potassium carbonate is raised, and the product becomes purer.

(4) Potassium chloride and sulphate, occurring native as minerals at Stassfurt, Germany, are, perhaps, the greatest sources of potassium carbonate at the present time. By a process similar to that of Leblanc, used in the preparation of sodium carbonate, these minerals are converted into a very pure carbonate. In

1892 the output of carnallite, containing 26.8 per cent. of KCl, was 736,750 tons, and of kainite, containing 35.1 per cent. of K_2SO_4, was 545,084 tons.

Properties.—Crude potassium carbonate, or potash, is in hard solid masses or coarse powder. The color varies from whitish, through gray-greenish and blue, to reddish-brown, according to the proportions of manganese and iron. The purer compound, known as pearlash, is white in color. All the different grades absorb moisture from the air, becoming damp and then liquid.

The commercial potash contains considerable quantities of other salts, chiefly potassium chloride, sulphate, and silicate, and sodium carbonate. There is also present more or less hydrate, depending on the method of manufacture.

The pure salt is official under the name of **Potassii Carbonas.** It is prepared by dissolving the impure salt in an equal weight of water, allowing to stand until the solution clears, and then decanting the clear, supernatant liquid on a filter; the filtrate is evaporated in an iron vessel until it thickens, when the heat is moderated, and with constant stirring the mass is brought to a dry, white, granular condition. In case the product does not respond to the official tests, the process should be repeated.

The chemically pure salt is prepared by making an intimate mixture of 2 parts of purified and finely-powdered potassium bitartrate with 1 part of similarly powdered and purified potassium nitrate. On bringing a hot piece of charcoal in contact with this mass, the latter ignites, a glow running through the whole of it. When this has ceased, heat is applied for some time in order to dissipate small quantities of cyanogen and ammonium compounds. The residue is dissolved in a small quantity of water, filtered, evaporated, and granulated. The operation in this case should be conducted in a silver dish. The product retains the name of *salt of tartar* to the present time, indicating the source from which it was at one time exclusively obtained. The pure salt may also be made by igniting crystallized potassium bicarbonate, as this salt is capable by crystallization of being prepared of a high degree of purity, a superior product may thus be obtained.

$$\underset{\substack{\text{Acid Potassium}\\ \text{Carbonate.}}}{2KHCO_3} = \underset{\substack{\text{Potassium}\\ \text{Carbonate.}}}{K_2CO_3} + \underset{\substack{\text{Carbon}\\ \text{Dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O}.$$

Properties.—Potassium carbonate is a white, dry, granular powder, without odor, and possessing a strongly alkaline taste

It is very deliquescent, absorbing moisture readily from the air; soluble in 1.1 parts of water at 15°, and in 0.65 part of boiling water; insoluble in alcohol. On heating to 130°, the salt loses the adhering moisture, which should not be more than 5 to 8 per cent., and at a red heat it melts, slowly volatilizing as the heat is increased to whiteness. The solution of the salt reacts strongly alkaline to litmus, and effervesces with acids.

From the concentrated aqueous solution crystals separate, having the formula $K_2CO_3.3H_2O$.

Potassium Bicarbonate, $KHCO_3$. **Potassii Bicarbonas, U.S.P.**—On passing carbon dioxide into a concentrated solution of the normal carbonate, the acid carbonate crystallizes out according to the following reaction:

$$K_2CO_3 + CO_2 + H_2O = 2KHCO_3.$$

The same result is sometimes accomplished by passing the carbon dioxide over the moistened pearlash. The product by either process is dissolved in water, filtered clear, and allowed to crystallize.

Properties.—Potassium bicarbonate occurs in colorless, transparent, monoclinic prisms. It is without odor, and has a saline and slightly alkaline taste. It is soluble in 3.2 parts of water at 15°, and in 1.9 parts at 50°. Above that temperature, in aqueous solution, it is rapidly decomposed into normal carbonate and carbon dioxide. It is insoluble in alcohol. When first dissolved in water the resulting solution has a neutral reaction, but on standing it becomes alkaline owing to the formation of the normal carbonate.

POTASSIUM AND CYANOGEN.

Potassium Cyanide, KCN.—This salt is prepared by taking an intimate mixture of 8 parts potassium ferrocyanide and 3 parts potassium carbonate, and projecting in small portions at a time into a red-hot iron crucible, when the following reaction takes place:

$K_4Fe(CN)_6$	+	K_2CO_3	=	$5KCN$	+	$KOCN$	+	CO_2	+	Fe.
Potassium Ferrocyanide.		Potassium Carbonate.		Potassium Cyanide.		Potassium Cyanate.		Carbon Dioxide.		Iron.

When effervescence has ceased, and the liquid has become clear, it is poured carefully into an iron dish to solidify.

The French process, which, it is claimed, will yield a purer product, consists in heating the potassium ferrocyanide alone with exclusion of air to a bright red heat:

$$\underset{\text{Potassium Ferrocyanide.}}{K_4Fe(CN)_6} = \underset{\text{Potassium Cyanide.}}{4KCN} + \underset{\text{Iron Carbide.}}{FeC_2} + \underset{\text{Nitrogen.}}{N_2}.$$

A portion of the melted mass can be poured off clear, and the black residue can be extracted with alcohol.

A chemically pure potassium cyanide is prepared by passing hydrocyanic acid gas into an alcoholic solution of potassium hydrate. The salt separates out as a white, crystalline powder.

Properties.—Potassium cyanide occurs either in white, amorphous, opaque pieces, or as a white, granular powder. It may be obtained in regular octohedrons by allowing the concentrated aqueous solution to evaporate over sulphuric acid at ordinary temperatures. When perfectly dry it is odorless, but as ordinarily found it has an odor of hydrocyanic acid, owing to the presence of moisture. Its taste is sharp, bitterish, and somewhat alkaline. The salt is soluble in 2 parts of water at 15°, and in an equal weight of boiling water; at the latter temperature, however, it is rapidly decomposed. It is sparingly soluble in alcohol. When exposed to damp air, the salt readily deliquesces. The aqueous solution has an alkaline reaction. When heated to low redness, the salt fuses, and, on cooling, solidifies in cubes. It is decomposed by the weakest acids, even carbonic acid being able to displace the hydrocyanic radical. Violent explosions occur when this salt is mixed with nitric acid or with potassium chlorate. Potassium cyanide is official under the name of **Potassii Cyanidum.** Its use in medicine is limited. In electro-metallurgy and in photography it is more extensively employed.

Potassium Cyanate, KCNO.—When equal parts of potassium ferrocyanide and manganese dioxide are intimately mixed, and fused until the mass begins to soften, potassium cyanate is formed. After allowing the mass to cool it is extracted with 80 per cent. alcohol, and this solvent, on cooling, deposits the salt in transparent tabular crystals. It is readily soluble in water and in alcohol. The salt in aqueous solution gradually decomposes into water and potassium bicarbonate. It is chiefly used in the preparation of organic compounds.

Potassium Thiocyanate, or Sulphocyanate, KCNS.—This salt is prepared by gently heating together 46 parts of potassium ferrocyanide, 17 parts of potassium carbonate, and 32 parts of sulphur. When the fused mass is cooled it is extracted with hot alcohol, and this solvent deposits the crystallized salt, on cooling, in long striated transparent prisms.

Potassium thiocyanate is very soluble in water and in alcohol. On account of the deep red color it produces with ferric salts, it becomes a delicate test for them.

SODIUM.

Symbol, Na. *Atomic Weight*, 23. *Valence*, I.

History.—As stated under the preceding element, the salts of sodium and potassium were not distinguished from each other until 1736. Those of sodium were probably the first known. *Nitrum*, which later came to be a name for saltpetre, was probably in earlier times applied to an impure sodium carbonate, since it effervesced on the application of vinegar. Sodium chloride, because of its presence in sea water, was known in the earliest times.

The metal sodium was discovered by Davy in 1807, in the same manner as potassium,—namely, by the electrolysis of the hydrate.

Occurrence.—Sodium, like the other alkali metals, is not found in nature in the free state; but in combination it is very widely distributed. Sodium chloride is found as rock-salt in the earth, it is a constituent of sea water, of the water of many mineral springs, and it is almost universally distributed in animal and vegetable organisms.

Sodium silicate is a constituent of albite, or soda-feldspar, and in smaller quantity in many other minerals. The nitrate, as Chili saltpetre, is found in the warm and rainless districts of Chili and Peru. Cryolite, found in large deposits in Greenland, is the double fluoride of sodium and aluminum. Sodium carbonate occurs as a natural deposit in the warm and rainless districts of many countries, notably in Egypt, India, South America, and in Wyoming and California; in the latter places, however, it is usually associated with larger quantities of sodium sulphate or borate. Smaller quantities of the sulphate and the iodide are found in sea water.

Preparation.—Sodium is produced by the electrolytic apparatus of Castner, described under potassium, Fig. 112. It is also manufactured on a large scale by a process of Castner, in which sodium hydrate and iron carbide are heated together to 800°, when sodium distils according to the following reaction:

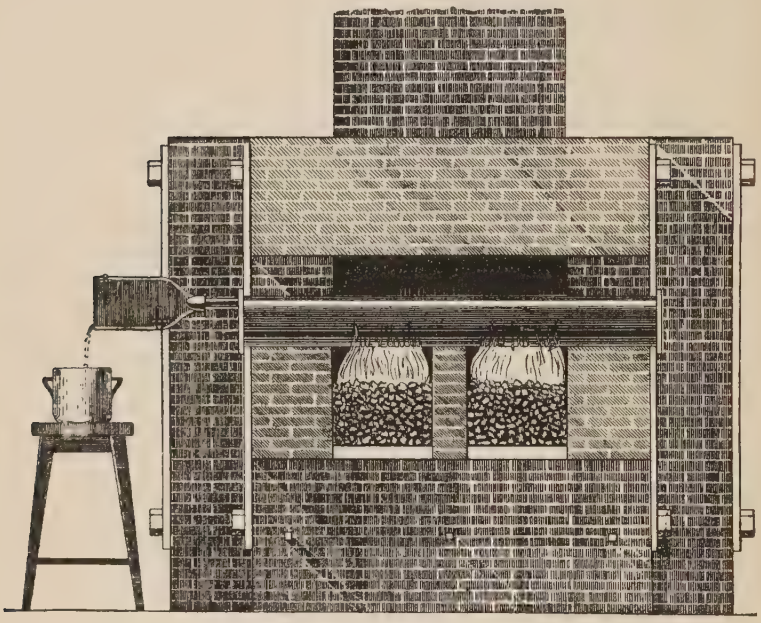
$$\underset{\text{Sodium Hydrate.}}{6NaOH} + \underset{\text{Iron Carbide.}}{FeC_2} = \underset{\text{Sodium Carbonate.}}{2Na_2CO_3} + \underset{\text{Hydrogen.}}{3H_2} + \underset{\text{Iron.}}{Fe} + \underset{\text{Sodium.}}{Na_2}.$$

The older method of Deville is still used considerably. This consists in heating an intimate mixture of sodium carbonate and carbon, when the following reaction occurs:

$$Na_2CO_3 + 2C = Na_2 + 3CO.$$

The apparatus by which this is accomplished is shown in Fig. 115. A charge for this apparatus consists of 30 kilogrammes of soda-ash, ground with 13 kilogrammes of small coal and 3 kilogrammes of chalk. This is placed in the cylinder A, which is

FIG. 115.



Sodium furnace.

1.2 meters long and 0.14 meter in diameter, and the whole is brought to a white heat. There is not the same danger from explosion that there is in the preparation of metallic potassium.

It has also been proposed to prepare sodium by electrolysis directly from the chloride, since both the metal and the chlorine are valuable; many suggestions have been made and a number of patents granted, but as yet the process does not appear to have become a success.

Properties.—Sodium is a silver-white metal, of a waxy consistence at ordinary temperatures, but in the cold it becomes brittle and crystalline. It has a specific gravity of 0.9735 at 13.5°.

On the application of heat sodium melts at 95.6°, and at 742° it boils; under these conditions it is necessary to exclude air. The metal is so easily oxidized at ordinary temperatures that it is necessary to preserve it under petroleum. If it is melted in the atmosphere of an inert gas like nitrogen, and when it begins to solidify the liquid portion is poured out, the remainder takes the form of octohedral crystals.

The behavior of sodium towards most other elements is similar to that of potassium, but less energetic; for instance, potassium and bromine combine with explosive violence, while sodium may be warmed with it without violent action.

When thrown on water, sodium combines with the oxygen of the water, liberating hydrogen, but the action is not sufficiently energetic to inflame the latter, unless the metal be held in one position by a piece of filter paper, or the water be warmed to 60°, when the gas ignites and burns with a yellow flame. This yellow color is characteristic of sodium compounds.

Uses.—Sodium is used in the preparation of a number of other metals, notably, silicon, boron, magnesium, and aluminum. It is also a valuable reducing agent in the laboratory. In some cases where its activity does not admit of its being used alone, as in aqueous solutions, it is first amalgamated with mercury.

SODIUM AND HYDROGEN.

Sodium Hydride, Na_4H_2.—When dry hydrogen is passed over sodium at a temperature of from 300° to 400° the metal absorbs 237 times its volume of the gas. The product has a silver-white color and a metallic lustre.

SODIUM AND HALOGENS.

The halogen compounds of sodium are:

Sodium fluoride, NaF.
Sodium chloride, NaCl.
Sodium bromide, NaBr.
Sodium iodide, NaI.

Sodium Fluoride, NaF, is prepared by neutralizing hydrofluoric acid with sodium carbonate. The compound crystallizes in anhydrous cubes. It is soluble in 25 parts of cold water, and scarcely more so in hot water. It has a tendency to form double compounds with other salts, as instanced in cryolite, the double fluoride of sodium and aluminum, $Al_2F_6 6NaF$.

Sodium Chloride, NaCl. **Sodii Chloridum**, U. S. P.—Sodium chloride, or common salt, is found abundantly throughout

the globe. As rock-salt it occurs in large deposits, alternating with strata of clay and gypsum, at an average depth of 100 meters. Probably the most celebrated mines are at Wieliczka, in Galicia, the deposit there being 500 miles long, 20 miles broad, and 1200 feet thick. Enormous quantities are also found in England, at Stassfurt, Germany, and in America.

Numerous salt springs also occur in many parts of the world, in which common salt is the chief constituent. These springs are especially abundant in West Virginia, Michigan, and New York, each containing a large number of these springs.

Sea water contains 3 to 4 per cent. of solid residue, three-fourths to nine-tenths of which is sodium chloride, or 2.4 to 2.8 per cent. of the sea water. There is relatively more salt in that part of the ocean situated near or crossed by the equator. Many inland seas contain a greater proportion of salt than exists in the ocean. For instance, the water of the Great Salt Lake in Utah contains over 22 per cent. of saline matter, about 90 per cent. of which is sodium chloride.

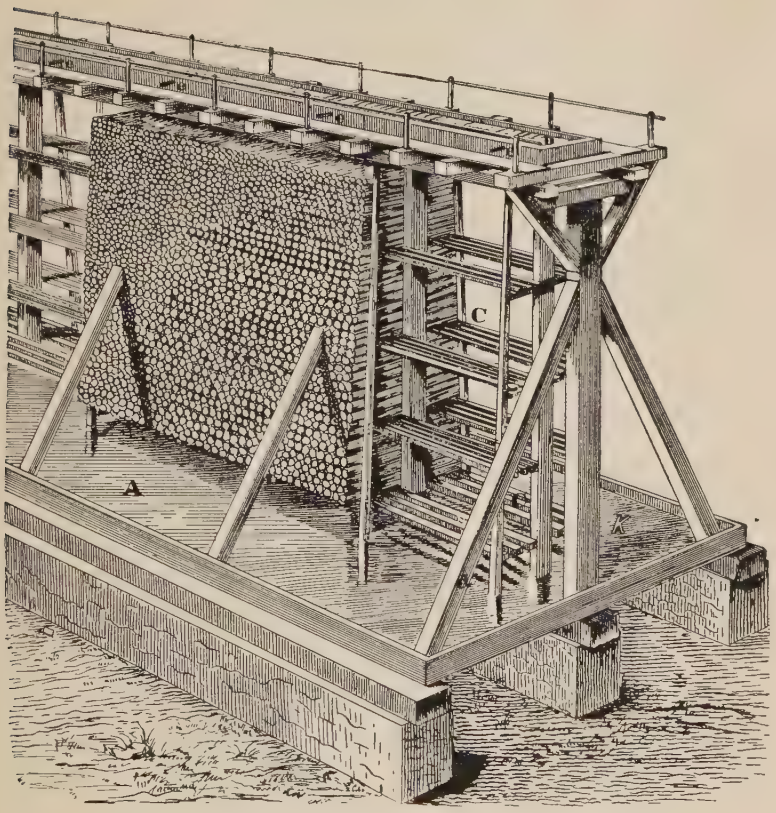
Extraction.—When sufficiently pure, rock-salt is mined and sent at once into commerce without further purification. If it is more inaccessible, or mixed with earthy matter, holes are drilled into the deposits, water is run in, and the saturated solution is either forced out by the water which enters, or it is pumped out. The salt is recovered by evaporating the solution in iron or lead boilers. Weaker salt solutions are first evaporated by the sun's rays. This is accomplished either in large shallow dikes lined with clay, as carried out with sea water in the south of France, or by allowing the solution to trickle down over a large pile of brushwood, as shown in Fig. 116. When the liquid has reached a concentration representing 15 to 20 per cent. of salt, it is run into open boilers and the evaporation completed.

The salt thus produced is quite impure and requires further treatment. In some cases it is spread on washed sand, and the more deliquescent salts liquefy and are absorbed ; in other cases the crude salt is placed in baskets over the boilers in which the brine is concentrating, the steam rising dissolves the more soluble salts. Finally, crude salt may be purified by washing it with a saturated solution of pure salt.

When a purer compound is desired for chemical purposes, the purest commercial salt is carefully treated with barium chloride solution so long as a precipitate is produced, by which the sodium sulphate is decomposed, barium sulphate and sodium chloride re-

sulting ; the barium sulphate is filtered out, and the warm filtrate is treated with a slight excess of sodium carbonate, this precipitates aluminum, barium, calcium, iron, and magnesium com-

FIG. 116.



Evaporation of weak brines.

pounds ; after filtering clear, the solution is carefully neutralized with hydrochloric acid, and evaporated to the crystallizing point.

The production of salt in the United States in 1897 was 14,455,783 barrels of 280 pounds, valued at $6,385,750. Upward of 90 per cent. of the production in 1897 was evaporated from brine, the remainder being the rock-salt production.

Properties.—Sodium chloride ordinarily occurs in transparent cubical crystals, or as a white, crystalline powder. It is permanent

in the air, odorless, and has a pure saline taste. Water dissolves 2.8 parts at 15°, and 2.5 parts at the boiling point; it is almost insoluble in alcohol. The solution in water has a neutral reaction. When heated the salt decrepitates; at a red heat (about 772°) it fuses, and at a white heat it is slowly volatilized with some decomposition.

Uses.—Sodium chloride is used as a condiment, in medicine, and as a source for the preparation of other sodium salts, the most conspicuous of which are sodium sulphate and carbonate.

Sodium Bromide, NaBr. **Sodii Bromidum,** U. S. P.—The preparation of this salt is carried out similarly to the potassium salt, either by double decomposition between ferrous bromide and sodium carbonate, or by the formation of sodium bromide and bromate by the combination of bromine and sodium hydrate. The bromate is converted into bromide by fusion with charcoal.

Properties.—Sodium bromide occurs in colorless or white cubical crystals; without odor, and with a saline, slightly bitter taste. The salt slowly attracts moisture from the air without deliquescing; this is probably due to the fact that at ordinary temperatures it crystallizes with two molecules of water, but as found in commerce it is free from water of crystallization, the latter condition having been attained by crystallizing from a warm solution, or above 30°.

Sodium bromide is soluble in 1.2 parts of water at 15°, and in 0.5 part of boiling water; in 13 parts of alcohol at 15°, and in 11 parts of boiling alcohol. When heated the salt melts at 712°, and at higher temperatures it is slowly volatilized with some decomposition.

Uses.—The principal use of sodium bromide is in medicine.

Sodium Iodide, NaI. **Sodii Iodidum,** U. S. P.—This salt is prepared almost exactly as the corresponding potassium salt.

Properties.—Sodium iodide occurs in colorless cubical crystals, or as a white, crystalline powder; it is odorless, and has a saline, slightly bitter taste. It is deliquescent in moist air, and when exposed decomposes into sodium carbonate and free iodine, thereby becoming reddish-brown in color.

The salt is soluble in 0.6 part of water at 15°, and in 0.33 part of boiling water; in 3 parts of alcohol, and in 1.4 part of boiling alcohol. When it crystallizes from water at ordinary temperatures it contains two molecules of water of crystallization, but above 40° it separates anhydrous. When heated it melts, and at

a higher temperature it volatilizes with some decomposition. Its aqueous solution is neutral to litmus paper.

Uses.—Sodium iodide has some use in medicine, as it is considered preferable to the potassium salt where its use is to be continued for some time.

SODIUM AND OXYGEN.

Sodium combines with oxygen in two proportions, resulting in the following well-defined compounds:

Sodium monoxide, Na_2O.
Sodium peroxide, Na_2O_2.

Sodium Monoxide is formed with some peroxide when sodium is burned in air. On heating to a high temperature the peroxide loses half of its oxygen, and the monoxide remains. It may also be obtained by heating together sodium hydrate and sodium:

$$NaOH + Na = Na_2O + H.$$

It is a gray mass with a conchoidal fracture. When brought in contact with water, violent action occurs with the formation of sodium hydrate.

Sodium Peroxide, Na_2O_2.—This compound is formed when sodium is heated in oxygen gas, until the weight becomes constant. It is also produced by the ignition of sodium nitrate.

Properties.—As found in commerce, sodium peroxide is a yellowish-white powder. It is very deliquescent. When thrown into water, considerable heat is evolved, and sodium hydrate and oxygen are formed, as follows:

$$Na_2O_2 + H_2O = 2NaOH + O.$$

When, however, a dilute acid is present, hydrogen dioxide results:

$$Na_2O_2 + 2HCl = 2NaCl + H_2O_2.$$

This compound has within the past few years become an article of commerce for bleaching and oxidizing purposes.

It contains about 20 per cent. of available oxygen.

Sodium Hydrate, **Soda**, U. S. P. (Sodium Hydroxide, Caustic Soda), NaOH.—The simplest method or forming the hydrate of sodium is by throwing the metal on water:

$$Na_2 + 2H_2O = 2NaOH + H_2.$$

This method requires considerable care, as the fused metal is

liable to be thrown about. It is employed when a very pure product is desired.

A cheaper and more usual method consists in dissolving 3 parts of sodium carbonate crystals in 15 parts of water, heating to the boiling point, and adding in small portions at a time milk of lime, obtained by slaking 1 part of quick-lime, calcium oxide, with 3 parts of water; this mixture is boiled for some time, water is added to replace that which is evaporated, until a portion of the clear liquid fails to give effervescence on the addition of dilute acid:

$$\underset{\text{Sodium Carbonate.}}{Na_2CO_3} + \underset{\text{Calcium Hydrate.}}{Ca(OH)_2} = \underset{\text{Sodium Hydrate.}}{2NaOH} + \underset{\text{Calcium Carbonate.}}{CaCO_3}.$$

The clear liquid is decanted from the precipitate and evaporated in an iron dish to a specific gravity of 1.170, when the concentration is completed in a silver dish and the fused product poured into silver moulds, similar to those used for potassium hydrate. (See Fig. 114.) On the commercial scale sodium hydrate is produced by a modification of the Leblanc process for preparing sodium carbonate by the addition of more coal in the black-ash fusion; the reaction being as follows:

$$CaCO_3 + C = CaO + 2CO.$$
$$Na_2CO_3 + CaO + H_2O = 2NaOH + CaCO_3.$$

Sodium hydrate is also obtained as one of the products in the electrolysis of common salt on a large scale. (See page 196.

That which is prepared in large quantities comes in commerce in iron drums; 54,331,533 pounds were imported in 1892.

Properties.—The sodium hydrate which is used for pharmaceutical and medicinal purposes occurs in dry, white, translucent pencils, showing a crystalline structure, free from odor, and having an acrid and caustic taste. When exposed to moist air it rapidly deliquesces; in dry air it first becomes coated with a dry film of carbonate. It is soluble in 1.7 parts of water at 15°, and in 0.8 part of boiling water; very soluble in alcohol.

On the application of heat sodium hydrate melts at 525° to a clear oily liquid, and at a bright red heat it is slowly volatilized unchanged. The solution, even when very dilute, gives a strongly alkaline reaction with litmus paper.

When sodium hydrate is free from water it has a specific gravity of 2.13. The very concentrated aqueous solution, when cooled to 0°, deposits crystals of the formula $NaOH.3\frac{1}{2}H_2O$. Water is always present in the commercial article; that coming in sticks

contains at least 10 per cent. of moisture. Alcohol is used to free the commercial compound from impurities, since the latter are of a character to be insoluble in this solvent. The commercial preparation, which has been purified by this means, is known as "soda by alcohol."

Liquor Sodæ, U. S. P., is made from sodium carbonate and lime according to one of the preceding processes, or else by dissolving 56 grammes of sodium hydrate (containing 90 per cent. of absolute NaOH) in sufficient water to make 1 liter. The resulting solution has a specific gravity of 1.059 at 15°, and contains about 5 per cent. of NaOH.

Uses.—Sodium hydrate is used externally as a caustic, and it is extensively employed as a chemical reagent. The most important technical use of the commercial product is in the preparation of soap.

OXYGEN SALTS OF SODIUM AND HALOGENS.

Sodium Hypochlorite, NaOCl.—This compound only occurs in solution. Officially it is known as **Liquor Sodæ Chloratæ**, or Labarraque's Solution. This solution is made by mixing solutions of sodium carbonate and chlorinated lime; the reaction is as follows:

$$\underset{\text{Chlorinated Lime.}}{Ca(ClO)_2 + CaCl_2} + \underset{\text{Sodium Carbonate.}}{2Na_2CO_3} = \underset{\text{Labarraque's Solution.}}{2NaClO + 2NaCl} + \underset{\text{Calcium Carbonate.}}{2CaCO_3}.$$

The clear supernatant liquid, after decantation, should contain 2.6 per cent. of available chlorine. This solution has a specific gravity of about 1.059 at 15°, and contains, in addition to the hypochlorite, sodium chloride and carbonate.

Sodium Chlorate, $NaClO_3$. **Sodii Chloras**, U. S. P.—Sodium chlorate may be prepared in the same manner as the corresponding potassium salt. On account of its greater solubility, however, its separation by crystallization is not so readily accomplished. It has been recommended, therefore, to prepare it for medicinal use by double decomposition between sodium bitartrate and potassium chlorate, the following reaction occurring:

$$NaHC_4H_4O_6 + KClO_3 = NaClO_3 + KHC_4H_4O_6.$$

For this purpose a concentrated solution of 19.5 parts of tartaric acid are added to 18.3 parts of crystallized sodium carbonate, previously dissolved in an equal quantity of hot water. The resulting

solution, while hot, is mixed with a hot solution of 16 parts of potassium chlorate in 50 to 60 parts of water. The whole is allowed to stand 24 hours for the potassium bitartrate to crystallize out. After filtering from the latter, the filtrate is evaporated carefully to dryness, dissolved in the smallest possible amount of water, filtered, and allowed to crystallize. As thus prepared, a pure product may, no doubt, be obtained, but, as a matter of fact, it is liable to be contaminated with tartaric acid. A process which yields a purer product consists in adding a hot solution of 9 parts of potassium chlorate to a similar solution of 7 parts of sodium silico-fluoride, and boiling :

$$2KClO_3 + Na_2SiF_6 = 2NaClO_3 + K_2SiF_6.$$

The subsequent treatment is the same as in the preceding process. The product in this case has the advantage of being free from the possible contamination with organic matter.

Sodium chlorate occurs in colorless, transparent crystals, or as a white, crystalline powder. Its taste is more decidedly saline and cooling than the corresponding potassium salt. It is soluble in 1.1 parts of water at 15°, and in 0.5 part of boiling water, in 100 parts of alcohol, and in 40 parts of boiling alcohol ; it is also soluble in 5 parts of glycerin. When heated, the salt melts and gives off oxygen, leaving a residue of sodium chloride.

On account of its greater solubility the salt has been used considerably in place of the potassium chlorate in calico printing and in the manufacture of aniline black.

Sodium Bromate, $NaBrO_3$, may, like the potassium bromate, be prepared during the manufacture of the corresponding bromide. It is soluble in about 3 parts of water at 15°. In other respects it resembles the potassium salt.

Sodium Iodate, $NaIO_3$, is prepared similarly to the preceding salt, and crystallizes with a variable proportion of water. It is soluble in some 14 parts of water.

SODIUM AND SULPHUR AND THEIR OXYGEN SALTS.

These compounds closely resemble the mono-, di-, tri-, and polysulphides of potassium, and may be prepared in a similar manner.

Sodium Hyposulphite, $NaHSO_2$.—This must not be confounded with the thiosulphate, $Na_2S_2O_3.5H_2O$, which is commercially known as hyposulphite.

The true sodium hyposulphite is prepared by reducing a concentrated solution of acid sodium sulphite in a well-corked bottle

with metallic zinc. The mixture is kept cool for about a half-hour, when a white precipitate of sodium zinc sulphite separates. The clear supernatant solution is then poured off into three times its volume of strong alcohol, and the resulting liquid poured into a bottle, completely filling it. The bottle is then tightly corked to exclude air, and set aside. A second crop of the sodium zinc sulphite crystals again forms, and the clear liquid is poured from these into a bottle, and excluded from the air as before. After some hours' standing, crystals of the sodium hyposulphite are seen to separate. They are filtered out, quickly pressed between folds of filtering paper, and dried in a vacuum. The resulting salt may be purified by solution in water and reprecipitation by alcohol as before.

This compound is used in dyeing, to reduce indigo, and as a laboratory reagent, where the estimation of free oxygen is involved.

Sodium Sulphite, $Na_2SO_3.7H_2O$. **Sodii Sulphis**, U. S. P.—Normal sodium sulphite is prepared by saturating a solution of sodium carbonate with sulphur dioxide, and then adding an amount of sodium carbonate, previously dissolved in water, equal to that first employed :

$$\underset{\text{Sodium Carbonate.}}{Na_2CO_3} + \underset{\text{Sulphur Dioxide.}}{2SO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Acid Sodium Sulphite.}}{2NaHSO_3} + \underset{\text{Carbon Dioxide.}}{CO_2}.$$

$$\underset{\text{Acid Sodium Sulphite.}}{2NaHSO_3} + \underset{\text{Sodium Carbonate.}}{Na_2CO_3} = \underset{\text{Sodium Sulphite.}}{2Na_2SO_3} + \underset{\text{Carbon Dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O}.$$

The solution is then carefully evaporated to crystallization.

If the solution be heated to the boiling point, the anhydrous sodium sulphite separates, and redissolves on cooling.

Properties.—The official salt occurs in colorless, monoclinic prisms ; it is without odor, and has a cooling, saline, somewhat sulphurous taste ; it effloresces when exposed to air, and is slowly oxidized to sulphate.

It is soluble in 4 parts of water at 15°, and in 0.9 part of boiling water ; it is scarcely soluble in alcohol. When the salt is gently heated, it softens somewhat, without fusing, and above 100° it loses its water of crystallization, amounting to 50 per cent., without the crystals changing their shape. At a red heat, the salt fuses to reddish-yellow masses of sodium sulphate and sulphide.

The aqueous solution is either neutral or faintly alkaline to litmus paper.

Acid Sodium Sulphite, $NaHSO_3$, **Sodii Bisulphis, U. S. P.**, is prepared, as stated under the preceding salt, when a solution of sodium carbonate is saturated with sulphur dioxide; the salt separates out in turbid crystals on cooling the solution.

Commercially it is much used in solution, from which, however, it may be crystallized, or precipitated by alcohol.

Properties.—The salt slowly evolves sulphur dioxide, and has a disagreeable, sulphurous taste. It is solubie at 15° in 4 parts of water and in 72 parts of alcohol, and in about 2 parts of boiling water and in 49 parts of boiling alcohol. When strongly heated, the vapors of sulphur and sulphur dioxide are evolved, and a residue of sodium sulphate remains. The aqueous solution imparts an acid reaction to litmus paper.

The official requirements demand a salt of 90 per cent. purity, but it is not often found in commerce of this strength.

Uses.—The salt and its solution are used largely as a preservative, and as a bleaching agent. Sulphur dioxide is readily and abundantly evolved on the addition of an acid.

Sodium Sulphate, $Na_2SO_4.10H_2O$. **Sodii Sulphas, U. S. P.**—The anhydrous salt is known as *salt-cake*, while the official compound with 10 molecules of water is known as *Glauber's salt*, after Glauber, who, in 1658, first described it under the name of *sal mirabile*. Sodium sulphate is widely diffused in nature. In the anhydrous condition it is found as the mineral thenardite, and in the hydrous form as mirabilite; the former is found in Spain and on Vesuvius, and the latter throughout the globe; it exists in sea water and in many mineral springs, chief of which is that at Carlsbad. Large amounts occur in a nearly pure state, in solution, in many lakes throughout the arid regions of western United States. A number of these lakes exist near Laramie, Wyoming, where the salt occurs in various degrees of purity, amounting in some cases to over 99 per cent.

Preparation.—In addition to being found native, sodium sulphate is a by-product in many chemical processes, and is also produced in enormous quantities as a preliminary step in the Leblanc process for manufacturing sodium carbonate. Large quantities are produced from the natural product in Wyoming; this natural product is dehydrated before sending into commerce. The official salt occurs in transparent monoclinic prisms or granular crystals, the commercial salt is frequently covered with efflorescence; it is without odor, and has a bitter, saline taste.

Sodium sulphate is soluble in 2.8 parts of water at 15°, and in 0.47 part of boiling water; at 34° water exerts the maximum solvent action, 1 part of the salt requiring 0.25 part of water; if this solution be heated, rhombic crystals of the anhydrous salt separate out.

Sodium sulphate fuses when heated to 33°, and at 100° it loses all its water, amounting to 55.87 per cent. At a red heat the anhydrous salt fuses without decomposition.

Uses.—Sodium sulphate has some use in medicine, but its greatest consumption is in the manufacture of sodium carbonate; it is also extensively employed in glass manufacture.

Acid Sodium Sulphate, $NaHSO_4$, is known as bisulphate of soda. It is prepared by heating 16 parts of sodium sulphate with 10 parts of pure concentrated sulphuric acid until they liquefy, and then dissolving the cooled, white, crystalline mass in twice its weight of water; by evaporating at 50° the anhydrous salt is obtained in triclinic prisms. When the crystallization takes place at the ordinary temperature, monoclinic prisms, with one molecule of water, $NaHSO_4.H_2O$, are formed.

There are other sodium sulphates of minor importance, which are very similar to the corresponding potassium salts, to which the reader is referred.

Sodium Thiosulphate, $Na_2S_2O_3.5H_2O$. **Sodii Hyposulphis, U. S. P.**—This salt is commercially, but incorrectly, known as hyposulphite of soda. It was discovered in 1799 by Chaussier.

Preparation.—Sodium thiosulphate is prepared by boiling a solution of sodium sulphite with sulphur:

$$Na_2SO_3 + S = Na_2S_2O_3.$$

The commercial source is from the *black ash* residue, after extraction of sodium carbonate in the alkali manufacture. When this residue is exposed to air for some time, the calcium sulphide, or oxysulphide, therein contained, is oxidized to thiosulphate, as follows:

$2CaS$	$+$	$2O_2$	$+$	H_2O	$=$	CaS_2O_3	$+$	$Ca(OH)_2$.
Calcium Sulphide.		Oxygen.		Water.		Calcium Thiosulphate.		Calcium Hydrate.

The thiosulphate is extracted from the mass with water, and the resulting solution decomposed with sodium sulphate as follows:

CaS_2O_3	$+$	Na_2SO_4	$=$	$Na_2S_2O_3$	$+$	$CaSO_4$.
Calcium Thiosulphate.		Sodium Sulphate.		Sodium Thiosulphate.		Calcium Sulphate.

Properties.—Sodium thiosulphate forms large, colorless, well-defined monoclinic crystals; odorless, with a saline, cooling,

afterwards bitter taste. It gives a neutral reaction, and is permanent in dry air. Above 33° it effloresces, and at 50° melts in its water of crystallization. At 100° it loses all its water, amounting to 36.26 per cent., and at a red heat it is decomposed, evolving sulphur which escapes, leaving a residue of sodium sulphate and sulphide.

Sodium thiosulphate is soluble in 0.65 part of water at 15° ; at the boiling temperature its solution is rapidly decomposed. It is insoluble in alcohol.

The chloride, bromide, and iodide of silver are readily soluble in solutions of sodium thiosulphate, forming a double salt as follows :

$$AgCl + Na_2S_2O_3 = NaAgS_2O_3 + NaCl.$$

Iodine is also dissolved by an aqueous solution of sodium thiosulphate, sodium iodide and tetrathionate being formed :

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$$

Chlorine acts in a similar manner, which fact has given to the salt the name of *antichlor ;* on this account it has extensive use in removing the excess of chlorine in bleaching operations. It is also used in photography, because of the property it possesses of dissolving the halogen compounds of silver.

OXYGEN SALTS OF SODIUM AND NITROGEN.

Sodium Nitrate, $NaNO_3$. **Sodii Nitras,** U. S. P.—In 1683 Bohn discovered this salt, which was more thoroughly investigated by Duhamel in 1736, and Marggraf in 1761. In 1820 it was first shipped from South America to European ports.

Occurrence.—Sodium nitrate is found as a natural deposit in parts of South America, chiefly in Chili, Peru, Bolivia, and the province of Bahia in Brazil. The Atacama Desert extends through the northern part of Chili into the southern part of Peru. It is in Atacama, Chili, Tarapaca, Peru, and the interlying region that the most extensive deposits occur. The district covers hundreds of miles, is practically rainless, and is especially favorable for the recovery of a salt like this, which is soluble in water. The crude deposit is termed "caliche," and one tract alone extends 40 miles in length, and 1 to 2 miles in width.

A characteristic nitrate *pampa*, or *calichero*, as it is called, consists of about the following strata : First, a layer of sand and gravel, about 1 to 2 inches deep ; then a 6-inch layer of a white friable substance consisting largely of calcium sulphate ; below

this is a stratum from 2 to 10 feet in thickness, consisting of earth and stones; then there is a layer 1 to 3 feet thick of a substance known as *costra*, which is low-grade *caliche*, composed of chlorides, feldspar, and earthy matter. The *caliche*, or crude sodium nitrate, lies below this; it forms a layer from 1½ to 2 feet in thickness. In the Tarapaca district this layer is much thicker, ranging from 4 to 12 feet. Below the sodium nitrate deposit is a stratum of fine clay 3 feet in depth, and resting on porphyritic rocks.

The value of the *caliche* varies from 15 to 65 per cent. sodium nitrate. The different grades are mixed so as to make an average product containing about 35 per cent.

Extraction.—The crude *caliche* is boiled with water until the liquor registers 110° Tw. at 120°, and the clear solution run into crystallizing tanks. The residue is boiled with water a second time, which usually completes the exhaustion. The liquor in the crystallizing tanks deposits its crystals of the nitrate in from 4 to 6 days, according to the temperature.

The mother liquor is then run off to the iodine house, where that valuable element is removed. The crystals of sodium nitrate are thrown out on draining-boards, washed once with a little cold water, allowed to dry, and are then packed in bags for shipment. As water is scarce in this dry region, all washings are saved and all steam is condensed as far as possible. In some places water is brought as far as 80 miles. The commercial sodium nitrate, prepared as above described, consists of 96 per cent. nitrate, with small quantities of chlorides, sulphates, moisture, and insoluble matter.

Properties.—For medicinal use the commercial salt would require purification by recrystallization. It is officially described as occurring in "colorless, transparent, rhombohedral crystals, odorless, and having a cooling, saline, and slightly bitter taste. Deliquescent in moist air. Soluble, at 15°, in 1.3 parts of water, and in about 100 parts of alcohol; in 0.6 part of boiling water, and in 40 parts of boiling alcohol."

When 75 parts of sodium nitrate are dissolved in 100 parts of water at 13.2°, the temperature falls to —5.2°.

On the application of heat, sodium nitrate melts at 312°, without decomposition; at a higher temperature it evolves oxygen and is converted into nitrite. The aqueous solution of the salt has a neutral reaction towards litmus paper.

Uses.—Sodium nitrate is used extensively as a fertilizer, as a

preservative agent for meat, and for the preparation of potassium nitrate by double decomposition with potassium chloride. Since it is cheaper than the potassium salt, it is used in the preparation of nitric acid. It cannot replace the potassium salt in the manufacture of gunpowder, because of its tendency to absorb moisture. The production of sodium nitrate on the west coast of South America in 1897 was 1,254,305 tons, of which 94,019 tons came to the United States.

Sodium Nitrite, $NaNO_2$, **Sodii Nitris**, U. S. P., is prepared by heating 100 parts of sodium nitrate with 285 parts metallic lead, in an iron vessel, to 500° :

$$NaNO_3 + Pb = NaNO_2 + PbO.$$

The fused mass is treated with water, filtered, and carbon dioxide passed through the filtrate in order to remove the last traces of lead. Finally, the salt is purified by repeated crystallization.

Properties.—As usually found in commerce, sodium nitrite is in opaque, fused masses or sticks. These have a yellowish-white color, and are made up of microscopic, prismatic crystals. The salt is odorless, has a mild, saline taste, and when exposed to the air deliquesces and is gradually oxidized to nitrate.

Sodium nitrite is soluble in about 1.5 parts of water at 15° ; very soluble in boiling water, and only slightly soluble in alcohol. On the application of heat, the salt melts, and at a red heat it decomposes, with the formation of oxygen, nitrogen, nitrogen dioxide, and sodium oxide. The aqueous solution reacts alkaline towards litmus paper.

This salt was made official because of its use in the manufacture of spirit of nitrous ether. The Pharmacopœia requires that it shall contain not less than 97.6 per cent. of the pure salt.

Sodium nitrite has considerable use as a chemical reagent, being usually employed when a soluble nitrite is demanded ; it is also employed by the color manufacturers.

OXYGEN SALTS OF SODIUM AND PHOSPHORUS.

Sodium Orthophosphates.—There are three compounds of sodium with orthophosphoric acid, as follows :

Trisodium orthophosphate, $Na_3PO_4.12H_2O$.
Disodium orthophosphate, $Na_2HPO_4.12H_2O$.
Monosodium orthophosphate, $NaH_2PO_4.H_2O$.

The first one of these, which is also known as the neutral sodium phosphate, is obtained when a slight excess of sodium

hydrate is added to the disodium salt or to orthophosphoric acid, and the solution evaporated. It separates in six-sided prisms, is easily soluble in water, and the resulting solution reacts alkaline towards litmus. When exposed to the air the solution absorbs carbon dioxide, sodium carbonate and the disodium salt resulting.

Disodium Orthophosphate, $Na_2HPO_4.12H_2O$.—This salt is official under the name of **Sodii Phosphas**, U. S. P., but is generally known in commerce as "phosphate of soda." It is widely distributed in the animal economy, especially in the urine, where it is found to the extent of from .3 to .5 per cent.

Sodium phosphate is formed when sodium carbonate is added to phosphoric acid until a faintly alkaline reaction is obtained. Below 33° crystallization takes place.

Properties.—These crystals contain 12 molecules of water, and rapidly effloresce on exposure to the air, losing 5 molecules of water (25.1 per cent.). They occur in large, colorless, monoclinic prisms, odorless, and having a cooling, saline taste. The salt is soluble in 5.8 parts of water at 15° and in 1.5 parts of boiling water; it is insoluble in alcohol.

On the application of heat, sodium phosphate fuses at 40°; at 100° it loses all its water of crystallization, amounting to 60.3 per cent., and at a red heat it is converted into sodium pyrophosphate. The aqueous solution reacts slightly alkaline towards litmus paper, but does not affect phenolphtalein.

Uses.—Sodium phosphate is used somewhat in medicine, largely as a reagent, and to a certain extent in the dyeing industry.

Monosodium Orthophosphate, $NaH_2PO_4.H_2O$.—When ordinary sodium phosphate and orthophosphoric acid are mixed and evaporated, the monosodium salt separates with one molecule of water of crystallization. These crystals occur in rhombic prisms, and their aqueous solution has an acid reaction.

Sodium Pyrophosphate, $Na_4P_2O_7.10H_2O$. **Sodii Pyrophosphas**, U. S. P.—The simplest method of obtaining this salt is by heating the ordinary sodium phosphate to 250°, or more rapidly by increasing the temperature to low redness, until a sample taken out and dissolved in water gives no yellowish color to the precipitate with silver nitrate. The following expresses the reaction:

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$

This operation may be conducted in an iron vessel, but one of silver is preferable. After the conversion is complete, the cooled

mass is dissolved in 5 parts of hot water, filtered, and the filtered solution allowed to crystallize.

Sodium pyrophosphate occurs in "colorless, transparent, monoclinic prisms, or a crystalline powder, odorless, and having a cooling, saline, and feebly alkaline taste." The crystals are permanent under most circumstances, but effloresce slightly in dry air.

The salt is soluble in 12 parts of water at 15°, and in 1.1 parts of boiling water; alcohol does not dissolve it. The aqueous solution is slightly alkaline to litmus and phenolphtalein. When heated to 100°, the salt loses its water of crystallization, amounting to 40.34 per cent. Above this temperature it fuses to a clear liquid, which solidifies in a crystalline mass.

Disodium Pyrophosphate, $Na_2H_2P_2O_7.6H_2O$, is prepared by heating the official sodium phosphate to 150° with strong hydrochloric acid, or by dissolving the normal pyrophosphate in acetic acid and precipitating by alcohol. As thus obtained, it occurs as a white, crystalline powder. Its aqueous solution has an acid reaction.

Sodium Metaphosphate, $NaPO_3$, is formed by heating the ordinary phosphate to bright redness for some minutes. This compound is scarcely soluble in water; it exists in several polymeric modifications, corresponding to the various polymeric metaphosphoric acids; these modified salts are more soluble in water.

Sodium Hypophosphite, $NaPH_2O_2.H_2O$. **Sodii Hypophosphis,** U. S. P.—Sodium hypophosphite is obtained by adding solution of sodium carbonate to one of calcium hypophosphite as long as a precipitate is produced. The filtered solution is evaporated at a low temperature, and concentration is completed in a vacuum. Dangerous explosions have resulted from too rapid evaporation of this solution, even a water-bath temperature may result disastrously.

Properties.—This salt occurs in pearly, tabular crystals, or in a white, granular powder; it is without odor, but possesses a bitterish-sweet, saline taste. It is very deliquescent on exposure to moist air, and the solution is neutral to litmus paper.

Sodium hypophosphite is soluble in 1 part of water and in 30 parts of alcohol at 15°; it is dissolved by 0.12 part of boiling water and by 1 part of boiling alcohol; in absolute alcohol it is slightly soluble, but insoluble in ether.

On carefully heating a small quantity of the salt in a test-tube, it first loses water of crystallization, and at 200° it is decomposed with the evolution of spontaneously inflammable hydrogen phosphide and some hydrogen, which burn with a yellow flame.

Sodium hypophosphite should not be triturated with nitrates, chlorates, permanganates, or other oxidizing agents, as violent explosions thereby result.

OXYGEN SALTS OF SODIUM AND BORON.

Sodium Borate, $Na_2B_4O_7.10H_2O$. **Sodii Boras**, U. S. P.

History.—Borax was known to the ancients and to the alchemists. Its true chemical character was not understood until 1747, when Baron pointed out the fact that it consisted of boric acid (then called sedative salt) and soda.

Occurrence.—Originally borax was known in certain lakes of Thibet, later it was brought from India and Persia, and was found in smaller quantities in various parts of the world. Rich deposits are found in the nitre regions of Chili and Peru, and in Ecuador. The abundant deposits of borax in the United States were not discovered until 1856, and not worked until 1864. The discovery appears to have been made by Dr. Veatch, at Clear Lake, California. Since that time numerous other deposits have been discovered in California and Nevada. In some of these localities the base is calcium instead of sodium ; in South America, for instance, the mineral *boronatrocalcite*, $Na_2B_4O_7.2CaB_4O_7.18H_2O$, is chiefly found, while the *borocalcite*, $CaB_4O_7.4H_2O$, is found in these as well as in many other places. One bed of this latter mineral, near Death Valley, in California, has an average depth of six feet. It is locally known as *colemanite*, from Coleman, the discoverer. This mineral is also known as *ulexite*, and, from the nature of the crystallizations, it is termed cotton-balls by the inhabitants.

Extraction.—Crude borax is known as *tincal*. This crude product in many cases only requires to be dissolved in water and allowed to crystallize in order to make it sufficiently pure to be sent into commerce. In other deposits there is much matter of a greasy nature, which must first be removed by washing with a weak solution of sodium or calcium hydrate. The deposits in this country, however, are of such purity as merely to require recrystallization. When *borocalcite* or *ulexite* is used, it is boiled with water and sodium carbonate, the result being sodium borate and calcium carbonate. Much of the borax formerly consumed in the Eastern Hemisphere was made by neutralizing the native boric acid of Tuscany with sodium carbonate. The production of borax in California and Nevada in 1897 was 18,000,000 pounds,

valued at $900,000, the entire output being handled by the Pacific Coast Borax Company, of San Francisco, California.

Properties.—Sodium borate occurs in colorless, transparent, prismatic crystals, or as a white powder; it is odorless, and has a sweetish, alkaline taste. In warm, dry air it is slightly efflorescent.

The salt dissolves in 16 parts of water at 15°, and 0.5 part of boiling water; it is insoluble in alcohol. At 80° it is soluble in 1 part of glycerin. On the application of heat, borax first loses a part of its water of crystallization, and, without melting, swells to a white, porous mass. When the heat is increased to redness, the remainder of the water is driven off, amounting to 47.14 per cent., and the salt fuses to a colorless liquid, which on cooling hardens to a transparent glass known as borax glass. The aqueous solution of the salt reacts alkaline towards litmus paper, and colors yellow turmeric paper brown.

Uses.—On account of its solvent action on metallic oxides, borax is largely used in soldering and welding. Its extended use in metallurgical operations and in blowpipe analysis is well known. It enters into the composition of some soaps, is used as a preservative, and is employed in the manufacture of certain kinds of glass, and in some enamels.

Octohedral Borax is a variety with 5 molecules of water of crystallization. It is formed by allowing crystallization to take place above 60°. This is accomplished by dissolving ordinary borax in boiling water until the solution has a specific gravity of 1.246, and then allowing it to cool slowly; the crystallization begins when the temperature reaches 79°. Below 56° ordinary prismatic borax crystallizes.

Sodium Metaborate, $NaBO_2.4H_2O$.—This salt is formed when 1 molecule of borax is fused with 1 molecule of sodium carbonate, the product is the anhydrous salt, which, when dissolved in water and allowed to crystallize, separates with 4 molecules of water.

Sodium Orthoborate, Na_3BO_3.—When boron trioxide is fused with sodium hydrate the following reaction takes place:

$$\underset{\text{Boron Trioxide.}}{B_2O_3} + \underset{\text{Sodium Hydrate.}}{6NaOH} = \underset{\text{Sodium Orthoborate.}}{2Na_3BO_3} + \underset{\text{Water.}}{3H_2O}.$$

This salt is very unstable, and cannot exist in solution, since it is converted by water into the metaborate.

OXYGEN SALTS OF SODIUM AND SILICON.

SODIUM SILICATES.

Sodium silicate is a constituent of many minerals and of glass. There are at least three compounds of silicic acid with sodium,

which are formed according to the proportion of the constituents entering into the reaction. When quantities of silica and sodium carbonate, equal to their respective molecular weights, are fused together, sodium metasilicate, Na_2SiO_3, is formed.

This compound is soluble in water, and when it is dissolved in that liquid and slowly evaporated, it separates in monoclinic crystals with 6 molecules of water of crystallization. If in the fusion an excess of sodium carbonate be used, the trisilicate, $Na_8Si_3O_{10}$, is formed.

Commercial sodium silicate, or *water glass*, consists chiefly of sodium tetrasilicate, $Na_2S_4O_9$. It is prepared by fusing together 45 parts of powdered quartz or fine sand, 23 parts of dry sodium carbonate, and 3 parts of charcoal. The fused product is run into a tank of water, which has the effect of converting it into small porous masses, which are more easily dissolved in water. The solution in water is a thick, viscid liquid, which forms the **Liquor Sodii Silicatis, U. S. P.** It is officially described as follows: "A semi-transparent, almost colorless, or yellowish, or pale greenish-yellow, viscid liquid, odorless, having a sharp, saline, and alkaline taste, and an alkaline reaction. Specific gravity, 1.300 to 1.400 at 15°."

Soluble glass is used largely as a bandaging material, enters into the composition of many cements, and is used in large quantities in the manufacture of silicated soaps.

Sodium Fluosilicate, Na_2SiF_6.—This compound is also known as sodium silicofluoride. It is prepared by neutralizing hydrofluosilicic acid with sodium hydrate or carbonate. Like the corresponding potassium salt, it is not very soluble in cold water. It is stated to have powerful antiseptic properties, and has been introduced into medicine under the name of "Salufer."

OXYGEN SALTS OF SODIUM AND CARBON.

Sodium Carbonate, $Na_2CO_3.10H_2O$. **Sodii Carbonas, U.S.P.**

History.—Sodium carbonate, or soda, has been known since the earliest times. It was not originally distinguished from potash, both being designated by the term *nitrum*.

Duhamel, in 1736, and Marggraf, in 1759, were the first to draw a sharp distinction between the two; the former showed the base of common salt, borax, and the ashes of sea plants to be one and the same; the latter designated soda as *mineral alkali*, and distinguished it from potash by the yellow color it imparted to the flame.

Nearly all the soda was obtained previous to 1793 from the ashes of sea plants, called *varec* or *kelp*. These sea-weeds were collected on the northwest coasts of France, Ireland, and Scotland.

One of the immediate results of the French Revolution was to cause a demand for soda from some other source than sea-weeds. On investigating the various processes, it was found that an apothecary, Nicolas Leblanc, associated with Dizé, was operating a small manufactory at St. Denis, in which he used sea salt to furnish the sodium for his sodium carbonate. The manufactory became a national establishment, and was successfully at work in 1794. Other manufactories by this process were more successful at Marseilles, and the original one was soon closed. The industry was established in England in 1823 by Muspratt.

There is probably no operation in the whole field of industrial chemistry that has undergone so few fundamental changes. So far as the material employed and the reactions involved are concerned, they remain the same as in the original process. It is true that many improvements have been introduced, but they have been of a mechanical nature or have related to the utilization of waste material. In more recent times entirely different processes have been established, the most successful ones being that by Thomsen (1851), in which *cryolite* is used, that by Solvay (1873), known as the *ammonia-soda* process, and the several processes which electrolyze sodium chloride.

Occurrence.—Sodium carbonate is found in the ash of all plants, but especially in that from sea plants and those growing near salt waters. It is also found in the waters of many mineral springs, often in the form of bicarbonate. An efflorescence or deposit, consisting largely of sodium carbonate, occurs in the soil in many rainless localities, as in Egypt, Mexico, parts of South America, and in the drier parts of the United States, there being unknown quantities in California, Wyoming, and Nevada, and probably in some other Western States. The native product in this country was produced to the amount of 3000 tons in 1896, valued at $65,000.

Preparation.—1. *Native Soda.*—The soda which occurs in nature consists almost entirely of the sesquicarbonate, having the formula $2NaHCO_3.Na_2CO_3.2H_2O$. That which is brought from Egypt is usually known as *Trona-soda*, that from South America (Colombia) and Mexico is called *Urao-soda*, and the small quantity brought into commerce from Hungary is known as *Szek*.

2. *Soda from the Ashes of Plants.*—The amount found in the ashes of sea and sea-coast plants is from 5 to 30 per cent. The soda from Spain is usually known as *Salsola soda* and *Barilla;* that from the south of France is called *Salicox* or *Blanquette* soda; and that prepared from the species of Fucus, used also in the preparation of bromine and iodine, is called *Kelp* soda in Scotland, and *Varec* soda in Normandy and the Channel Islands. Potassium is far more widely distributed in plants than sodium, but those plants growing in or near the salt water take up large quantities of sodium chloride and convert it into salts of the organic acids.

3. *The Leblanc Process.*—When sodium carbonate is manufactured by this method, the first step consists in converting sodium chloride into sulphate; this part of the operation is known as the salt-cake process. It consists in decomposing the sodium chloride in a furnace, as shown in Fig. 99, page 202, with chamber acid (sulphuric acid having a specific gravity of 1.60 to 1.70). In many works a double furnace is used, as shown in Fig. 117. The charge of salt, usually amounting to several hundred pounds, is placed in the central pan, and an equal quantity of the sulphuric acid is run in; there is an immediate evolution of large quantities of hydrochloric acid, according to the following reaction:

$NaCl$	$+$	H_2SO_4	$=$	$NaHSO_4$	$+$	$HCl.$
Sodium Chloride.		Sulphuric Acid.		Acid Sodium Sulphate.		Hydrochloric Acid.

The central pan in which this reaction takes place is of iron, and is heated by a fire underneath. The hydrochloric acid is passed into coke towers (see Fig. 100, page 203) to be condensed and dissolved by cold water, forming the commercial hydrochloric or muriatic acid. The residue in the pan consists of acid sodium sulphate with some undecomposed chloride. At the expiration of about an hour the mass is raked into one of the hearths or roasters on either side; here the reaction is completed by the higher heat from the furnaces at each end:

$NaHSO_4$	$+$	$NaCl$	$=$	Na_2SO_4	$+$	$HCl.$
Acid Sodium Sulphate.		Sodium Chloride.		Sodium Sulphate.		Hydrochloric Acid.

The hydrochloric acid which is evolved, is recovered as in the preceding part of the operation. The salt which remains consists of about 95 per cent. sodium sulphate, with small quantities of the acid sulphate, sodium chloride, calcium sulphate, ferric oxide,

and insoluble matter ; it is commercially known as *salt-cake*, or frequently simply as *sulphate*.

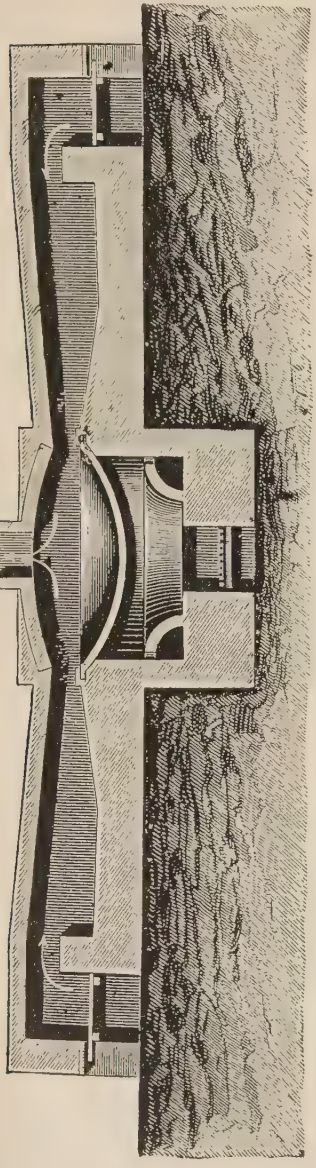


FIG. 117. Salt-cake furnace.

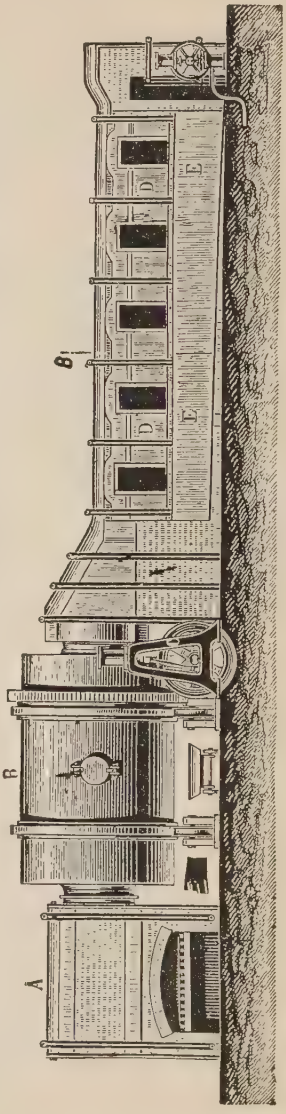


FIG. 118. Revolving black-ash furnace.

The sulphate is converted into carbonate by the *black-ash process*. This operation consists in fusing an intimate mixture

of salt-cake, calcium carbonate or limestone, and coal. The reaction takes place by two steps, as follows :

$$\underset{\text{Sodium Sulphate.}}{Na_2SO_4} + \underset{\text{Carbon.}}{4C} = \underset{\text{Sodium Sulphide.}}{Na_2S} + \underset{\text{Carbon Monoxide.}}{4CO.}$$

The sodium sulphate is first reduced to sulphide, and the latter reacts with the calcium carbonate, forming calcium sulphide and sodium carbonate :

$$\underset{\text{Sodium Sulphide.}}{Na_2S} + \underset{\text{Calcium Carbonate.}}{CaCO_3} = \underset{\text{Sodium Carbonate.}}{Na_2CO_3} + \underset{\text{Calcium Sulphide.}}{CaS.}$$

The above process was formerly carried out in an ordinary reverberatory furnace, but now nearly all works have adopted a revolving furnace, as shown in Fig. 118. The charge is introduced into the cylinder B from cars above, and, after fusion from the heat of the furnace A, is run out into cars beneath. The heat from A is introduced through the axle into the cylinder, and the excess passes out through the other side, to be used as presently described. These revolving furnaces accomplish by mechanical means what was formerly very difficult and costly labor,—namely, thorough mixing of the material during heating. The cylinder is revolved very slowly at first, and finally not faster than one revolution in three minutes. The quantities of the different materials employed by Leblanc were 100 parts each of salt-cake and limestone and 50 parts coal. In some works at the present time this proportion is only varied by using a relatively smaller amount of coal, but in some other manufactories there are employed 142 parts salt-cake, 100 parts limestone, and 24 parts coal.

These revolving furnaces are made of wrought iron and lined with fire-brick.

Crude soda or black ash has about the following composition :

	Per cent.
Sodium carbonate	45
Calcium sulphide	30
Calcium oxide	10
Calcium carbonate	5
Foreign matter	10

Considerable quantities of this crude soda are used without further purification in the manufacture of green glassware, in soap-making, and in bleaching.

The next step in the Leblanc process consists in lixiviating the black ash, evaporating the solution, and crystallizing. The black

ash is allowed to weather for a short time, by which it becomes more porous and more easily broken into small pieces ; it is then treated with water in such a manner as to effect solution with the least possible amount of liquid.

The solution is evaporated in the pans D, D, Fig. 118, by the waste heat from the furnace. The crystals which separate are raked out into E, E. These crystals are sometimes dissolved in water and recrystallized, by which they become crystal soda, or, as is much oftener the case, they are calcined on the hearth of a reverberatory furnace, and become raw soda or soda ash.

The mother liquor from the first crystallization of the soda contains considerable quantities of sodium hydrate ; it also contains some chloride, sulphate, cyanide, and sulphide as impurities. These are in part gotten rid of by allowing the liquor to run down a coke tower in which it meets a current of air ; the latter oxidizes the sulphides and cyanides. The liquor is then concentrated until it has a specific gravity of 1.10, when it is boiled with calcium hydrate, which removes carbonates and sulphates ; after they settle out, the clear liquor is drawn off into an iron vessel, evaporated, and heated to redness, when, after treatment with a little sodium nitrate to remove all cyanides, the caustic alkali is run into iron drums and sent into commerce.

Modifications of the Leblanc Process.—While many suggestions have been made regarding improvements of the Leblanc process, comparatively few have come into use. That devised by Hargreaves and Robinson involves an important change in the preparation of salt-cake. It consists in acting directly on sodium chloride by sulphurous oxide, oxygen (atmospheric), and watery vapor. The reaction is as follows :

SO_2	+	O	+	H_2O	+	$2NaCl$	=	Na_2SO_4	+	$2HCl$.
Sulphur Dioxide.		Oxygen.		Water.		Sodium Chloride.		Sodium Sulphate.		Hydrochloric Acid.

The sulphur dioxide is furnished directly from iron pyrites by roasting. The result is a purer product at a lower cost, but the increased expense of installation, greater consumption of fuel, and increased outlay for labor have been impediments to its general adoption.

Most of the other changes which have met with favor have related to utilization of the waste materials. These have mostly been in the direction of recovering the sulphur. This waste consists chiefly of calcium sulphide and carbonate, with small quantities of a number of other compounds.

By Chance's process 90 per cent. of the sulphur is recovered, and used as such, or converted into sulphur dioxide, to be used again in the production of sodium carbonate. The process consists in treating the alkali waste with carbon dioxide from lime-kilns. In the presence of moisture the following reaction takes place :

$$\underset{\text{Calcium Sulphide.}}{2CaS} + \underset{\text{Carbon Dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Calcium Carbonate.}}{CaCO_3} + \underset{\text{Calcium Sulphydrate.}}{Ca(SH)_2}.$$

With a further addition of carbon dioxide calcium carbonate is formed, with evolution of hydrogen sulphide, as follows :

$$\underset{\text{Calcium Sulphydrate.}}{Ca(SH)_2} + \underset{\text{Carbon Dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Calcium Carbonate.}}{CaCO_3} + \underset{\text{Hydrogen Sulphide.}}{2H_2S}.$$

This hydrogen sulphide is either burnt to SO_2 and used in the preparation of sulphuric acid, or the quantity of air with which it is heated is regulated so that free sulphur is formed as follows :

$$H_2S + O = H_2O + S.$$

A part of the alkali waste is utilized in the production of sodium thiosulphate, as described under that salt.

4. *Soda by Electrolysis.*—When anodes and cathodes are placed in a solution of sodium chloride, with porous diaphragms between them in such a way as to form water-tight compartments, and the electric current is passed, chlorine is generated in all the positive compartments and sodium in all the negative ones. The reaction is as follows :

$$\underset{\text{Sodium Chloride.}}{2NaCl} = \underset{\text{Sodium.}}{Na_2} + \underset{\text{Chlorine.}}{Cl_2}.$$

The chlorine is utilized for the production of bleaching powder. The sodium reacts with the water, producing sodium hydrate.

Carbon dioxide from lime-kilns is then passed into the solution of sodium hydrate, and sodium carbonate forms as follows :

$$\underset{\text{Sodium Hydrate.}}{2NaOH} + \underset{\text{Carbon Dioxide.}}{CO_2} = \underset{\text{Sodium Carbonate.}}{Na_2CO_3} + \underset{\text{Water.}}{H_2O}.$$

5. *The Ammonia-Soda Process.*—As long ago as 1838 this process was patented by Dyer and Hemming, but was first conducted on a commercial scale in 1855 by Schlössing and Rolland near Paris. The numerous practical difficulties, however, were not overcome until Solvay, in 1861, established a manufactory

near Brussels. Since that time it has slowly encroached on the Leblanc process, so that in 1892 the official figures for the output by these processes were as follows :

	Tons.
Leblanc soda	519,593
Ammonia-soda	304,897
Total	824,490

Leblanc soda does not appear to be produced in the United States, except, perhaps, the relatively small amount from the natural sodium sulphate in Wyoming, while the production of ammonia-soda by the Solvay patent amounted to 82,000 tons in 1892.

The ammonia-soda process consists in decomposing a saturated solution of sodium chloride with acid ammonium carbonate as follows :

$$\underset{\text{Sodium Chloride.}}{NaCl} + \underset{\text{Acid Ammonium Carbonate.}}{NH_4HCO_3} = \underset{\text{Acid Sodium Carbonate.}}{NaHCO_3} + \underset{\text{Ammonium Chloride.}}{NH_4Cl.}$$

In practice this is effected by running the salt solution down through a column, which meets in its descent the ammonia gas. This apparatus in which the brine is saturated is either iron, tin lined, or wood lined with lead. The ammonia enters through a perforated iron plate, by which it is broken up into small bubbles. Considerable rise of temperature takes place during the absorption, and the saturated brine is passed through a cooler into another vessel, in which it is saturated with the carbon dioxide. The reaction may be summed up as follows :

$$\underset{\text{Sodium Chloride.}}{NaCl} + \underset{\text{Ammonia.}}{NH_3} + \underset{\text{Carbon Dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Acid Sodium Carbonate.}}{NaHCO_3} + \underset{\text{Ammonium Chloride.}}{NH_4Cl.}$$

The ammonia is produced from ammonium chloride and calcium or magnesium oxide. Originally the calcium compound was employed, but by using the magnesium compound magnesium chloride is formed, which may be decomposed by steam with the production of hydrochloric acid and magnesium oxide. The process thus becomes a continuous one, in which the ammonia and magnesia are repeatedly used over, while the fresh materials required are common salt and carbon dioxide ; the latter is obtained from the lime-kilns, from magnesite, or from fuel.

The sodium bicarbonate produced in this process is collected

on a vacuum filter, washed with a small quantity of cold water, and dried. It is converted into normal carbonate by heat:

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

The carbon dioxide is used to furnish a part of that required to saturate the ammoniacal brine.

6. *Soda from Cryolite.*—The mineral cryolite occurs in enormous deposits in Greenland. The product of these mines is brought to Philadelphia and converted into sodium carbonate and bicarbonate at the works of the Pennsylvania Salt Company in Western Pennsylvania. This mineral has the composition $Al_2F_6.6NaF$, and is therefore a double fluoride of sodium and aluminum. When the finely-divided mineral is mixed with chalk or limestone and heated, the following reaction takes place:

$Al_2F_6.6NaF$	+	$6CaCO_3$	=	$Al_2O_3.3Na_2O$	+	$6CaF_2$	+	$6CO_2$.
Cryolite.		Calcium Carbonate.		Sodium Aluminate.		Calcium Fluoride.		Carbon Dioxide.

The fused mass is treated with water, whereby the soluble sodium aluminate is dissolved; carbon dioxide is then passed through this solution under pressure, which precipitates the aluminum hydrate and forms sodium carbonate:

$Na_6Al_2O_6$	+	$3CO_2$	+	$3H_2O$	=	$3Na_2CO_3$	+	$Al_2(OH)_6$.
Sodium Aluminate.		Carbon Dioxide.		Water.		Sodium Carbonate.		Aluminum Hydrate.

The clear solution is run off from the precipitate, and the sodium carbonate allowed to crystallize. A considerable portion of this company's output is converted into bicarbonate.

Properties.—When containing its full 10 molecules of water of crystallization, sodium carbonate occurs in large, colorless, monoclinic crystals, which have a specific gravity of 1.440 at 15°. The salt is odorless, and has an alkaline taste and reaction. When exposed to air the crystals become white, and gradually crumble to a fine white powder, losing about one-half of their water of crystallization, amounting to 31.46 per cent. The salt dissolves in 1.6 parts of water at 15°, and in 0.2 part of boiling water; it is most soluble at 38°, 0.09 part of water at that temperature being sufficient to dissolve 1 part of the crystals. The salt is insoluble in alcohol and ether, but soluble in 1.02 parts of glycerin. On the application of heat the crystals melt in their water of crystallization at 32.5°, and at 80° and above they lose all their water, amounting to about 63 per cent. The salt fuses at a bright red heat, or about 814°. When sodium and potassium carbonates are taken in the proportion of their

molecular weights, the mixture fuses at a considerably lower temperature than will either singly.

Sodium carbonate is perhaps used in larger quantity and in a greater variety of ways than any other alkaline salt. In addition to being employed itself, it forms the base from which many other sodium salts are prepared.

Pure sodium carbonate is prepared by dissolving the commercial crystals in one-half their weight of water at 30° to 40°, filtering the solution, and allowing it to stand in a cool place. The small crystals which separate are collected in a funnel, allowed to drain well, and then washed with a small quantity of cold water, or with a saturated solution of pure sodium carbonate. It may also be obtained by washing sodium bicarbonate with cold water, drying, and heating the residue to redness.

The impurities in the commercial carbonate are sodium chloride and sulphate, with perhaps ammonium salts.

Dried Sodium Carbonate. **Sodii Carbonas Exsiccatus,** U. S. P.—This is obtained from the commercial crystals by allowing them to effloresce at a temperature not exceeding 25° until they disintegrate, and then drying at 45° until they have lost one-half their weight.

Sodium Bicarbonate (*Acid Sodium Carbonate*). **Sodii Bicarbonas,** U. S. P.—This salt was first prepared by Valentine Rose in 1801. It occurs in many mineral waters, especially those of Ems and Vichy.

Preparation.—Sodium bicarbonate was originally prepared by passing carbon dioxide into a concentrated solution of neutral sodium carbonate; the bicarbonate, on account of its sparing solubility, separates out:

$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3.$$

Since the solution absorbs carbon dioxide slowly, the commercial process consists in making an intimate mixture of 4 parts of the effloresced carbonate and 1 part of the crystals. This mixture is distributed on broad shelves in a room, and carbon dioxide from some cheap source is passed in until the salt is saturated. Large quantities of the bicarbonate are now produced in the ammonia-soda process for making the neutral carbonate, and this furnishes a satisfactory product provided ammonium salts are removed. The cryolite process for the neutral carbonate also furnishes a superior bicarbonate; and these two sources now nearly supply the American markets, since the importations of 20,000,000

pounds annually some twenty years ago have decreased to less than 2,000,000 at the present time.

Properties.—Sodium bicarbonate forms in small monoclinic, tabular crystals, which are frequently united into crusts. As found in the shops, it is a white, opaque powder, permanent in the air under ordinary circumstances, but decomposing slowly in moist air. It has a mildly alkaline taste, and the cold solution, when freshly prepared, gives a faintly alkaline reaction to litmus paper.

The crystals have a specific gravity of 2.22 at 16°. The salt is soluble in 11.3 parts of water at 15°, and at a higher temperature, in the presence of water, it loses carbon dioxide, the neutral carbonate being formed; at the boiling temperature it is entirely converted into the neutral salt. Sodium bicarbonate is insoluble in alcohol and in ether.

On the application of heat, carbon dioxide and water are given off, with the formation of the neutral carbonate, as follows:

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

The reaction may be completed at 70°, although it takes place more rapidly at 100°, and when complete there is a loss of 36.3 per cent.

Uses.—Sodium bicarbonate enters into the composition of most baking powders; it is used as a cheap source of carbon dioxide in the preparation of effervescent drinks; and it has considerable use in the textile industries, especially in ungumming silk and scouring wool, as it attacks the fibre less than soap or ammonia.

AMMONIUM.

Formula, NH_4. *Molecular Weight,* 18.01. *Valence,* I.

History.—The salts of ammonium were known to the an cients, but ammonia gas was first collected by Priestley in 1774, although it was previously known that a pungent odor was developed on adding an alkali to sal ammoniac. Berthollet, in 1785, determined it to be composed of nitrogen and hydrogen.

Theoretical Considerations.—The present theory concern ing ammonium salts is that the compound NH_4 is a metal-like body which combines with the acids in the same manner that sodium and potassium do. This view has been strengthened by the formation of an amalgam composed of the radical NH_4 and mercury. When ammonium chloride, in contact with mercury, is subjected to the electric current, a bulky, buttery mass is formed

which is considered to be ammonium amalgam. The same product is obtained by placing sodium amalgam containing 1 per cent. of sodium in a concentrated solution of ammonium chloride, adding at the same time a few fragments of the salt. The bulky amalgam which is formed becomes crystalline at very low temperatures, and at —29° begins to decompose, forming 2 volumes of ammonia gas and 1 volume of hydrogen. The salts of ammonium most closely resemble those of potassium, with which they are isomorphous.

Occurrence and Sources.—The salts of ammonium are widely distributed in nature. The carbonate, nitrate, and nitrite are found in small quantities in the atmosphere, in rain, and in snow; the chloride is found in many volcanic gases; many of the above, as well as other compounds of ammonium, are found in the soil, and in the secretions of plants and animals.

One of the chief inorganic sources of ammonium salts is the native carbonate in the guano deposits of South America; the salt which exists in this guano is the acid carbonate, NH_4HCO_3.

The suffoni of Tuscany yield, besides boric acid, a considerable quantity of ammonium sulphate; in one locality four suffoni yield some 1500 kilos of ammonium sulphate in 24 hours. This salt is supposed to have resulted from the decomposition of organic matter in the Tuscan mountains, since the soil in the vicinity of the lagoons is impregnated with ammonium sulphate.

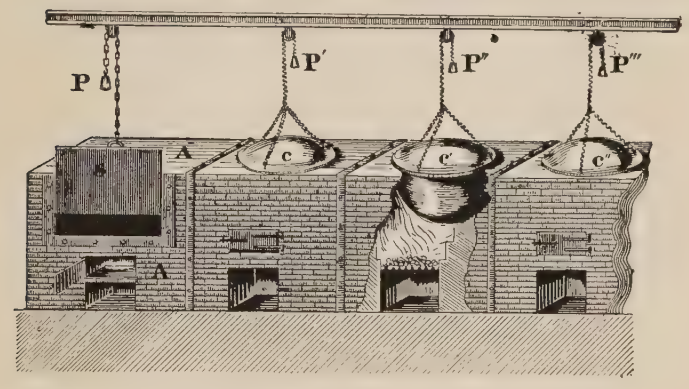
The organic sources of ammonium salts are of the greatest importance, and yield nearly all of the commercial salts; of these stale urine and the product from the distillation of bones formerly played an important part, but at the present time practically the entire supply comes from gas-liquor, from the condensed gases of coke-ovens and iron-works, and from the watery distillate of shale-works. These various ammoniacal liquors are treated according to the salt required, usually the chloride or sulphate, the details of which will be considered under the respective salts.

HALOGEN SALTS OF AMMONIUM.

Ammonium Chloride, NH_4Cl (Sal Ammoniac). **Ammonii Chloridum**, U. S. P.—Sal ammoniac was prepared in earlier times in Egypt by the sublimation of the ashes and soot resulting from the burning of camel's dung, which was there used as fuel. The salt may be prepared by the direct union of equal volumes of the gases, ammonia and hydrochloric acid.

At the present time the ammoniacal water from gas-works or similar sources is neutralized with hydrochloric acid, or oftener the ammonia gas is liberated from these liquors by lime and passed into the hydrochloric acid. The salt is first partly purified by crystallization, and then it is sublimed. This operation is usually conducted in cast-iron vessels (Fig. 119) lined with fire-

FIG. 119.



Sublimation of ammonium chloride.

clay, the dome sometimes being of earthenware or glass. The crude salt is rammed in tightly, and then heat is applied, gently at first in order to drive off moisture; a small hole is left in the top of the dome to allow the escape of this moisture. When the cake of sublimed salt in the dome has reached a sufficient thickness,—from 6 to 12 centimeters, according to the size of the caldron,—the dome is raised and the cake removed. When prepared in iron vessels sal ammoniac is usually contaminated with some of that metal; this may be prevented by adding to the charge, before subliming, about 5 per cent. of calcium phosphate, by which means any ferric chloride is decomposed and remains behind as phosphate. The crystalline and granular ammonium chloride is prepared by adding to the powdered salt a hot, saturated solution of the same, so as to form a magma of crystals, which are placed in moulds similar to those used in the manufacture of loaf-sugar; after thorough draining, the whole is dried, and the loaf of the salt is removed and packed for shipment. A former official process consisted in adding to a solution of the salt a little ammonium hydrate, filtering, evaporating, and granulating; this process was for the purpose of removing iron.

Properties.—Ammonium chloride comes in commerce as *sublimed sal ammoniac*, in concavo-convex cakes of fibrous crystals, or else as *crystallized sal ammoniac*, in the form of small, white octohedra or cubes. The salt is odorless, with a cooling, saline taste, and permanent in the air. It is soluble in 3 parts of water at 15°, and in 1 part of boiling water, but almost insoluble in alcohol. On the application of a low red heat, the salt is completely volatilized without residue. Its aqueous solution is neutral to litmus paper.

Ammonium chloride reacts slightly acid towards phenolphtalein, and as this property is characteristic of the other ammonium salts, this indicator cannot be used in their presence.

Uses.—Ammonium chloride is used extensively as a medicinal agent, for soldering, in calico printing and dyeing, and in the manufacture of a number of pigments; considerable quantities are also used as a reagent in the laboratory.

Ammonium Bromide, NH_4Br. **Ammonii Bromidum, U.S.P.**—This salt is prepared by neutralizing hydrobromic acid with ammonium hydrate or carbonate:

NH_4OH	+	HBr	=	NH_4Br	+	H_2O.
Ammonium Hydrate.		Hydrobromic Acid.		Ammonium Bromide.		Water.

It is also made by decomposing ferrous bromide with ammonium hydrate:

$FeBr_2$	+	$2NH_4OH$	=	$2NH_4Br$	+	$Fe(OH)_2$.
Ferrous Bromide.		Ammonium Hydrate.		Ammonium Bromide.		Ferrous Hydrate.

The ferrous hydrate is bulky and not completely precipitated until the solution is boiled, by which it is converted into ferric hydrate, $Fe_2(OH)_6$.

Properties.—Ammonium bromide occurs in colorless, transparent, prismatic crystals, or as a white, crystalline powder; the latter is made up of minute cubes. It is odorless, has a pungent, saline taste, and has a slightly acid reaction towards litmus paper. When exposed to the air, the salt undergoes slight decomposition, becoming of a yellowish color. It is soluble in 1.5 parts of water at 15° and in 0.7 part of boiling water, in 30 parts of alcohol at 15°, and in 15 parts of boiling alcohol. When heated, the salt volatilizes completely without melting.

Uses.—The chief use of ammonium bromide is in medicine, where in many cases it replaces potassium bromide with advantage.

Ammonium Iodide, NH_4I. **Ammonii Iodidum**, U. S. P.—The simplest method of preparing this salt is by neutralizing hydriodic acid with ammonia :

$$\underset{\text{Ammonium Hydrate.}}{NH_4OH} + \underset{\text{Hydriodic Acid.}}{HI} = \underset{\text{Ammonium Iodide.}}{NH_4I} + \underset{\text{Water.}}{H_2O.}$$

Hydriodic acid is prepared with some difficulty and expense, so that other methods have been tried with moderate success ; in one of these powdered iodine is added to freshly prepared ammonium sulphydrate, forming ammonium iodide, hydrogen sulphide, and sulphur :

$$\underset{\text{Iodine.}}{I_2} + \underset{\text{Ammonium Sulphydrate.}}{2NH_4HS} = \underset{\text{Ammonium Iodide.}}{2NH_4I} + \underset{\text{Hydrogen Sulphide.}}{H_2S} + \underset{\text{Sulphur.}}{S.}$$

It has been found impossible to remove all sulphur from the iodide in this process.

The following method was official in the U. S. Pharmacopœia of 1870 : Concentrated hot solutions of 33 parts potassium iodide and 13 parts ammonium sulphate are mixed, stirred well, mixed with alcohol, and the whole cooled to 40° :

$$\underset{\text{Potassium Iodide.}}{2KI} + \underset{\text{Ammonium Sulphate.}}{(NH_4)_2SO_4} = \underset{\text{Ammonium Iodide.}}{2NH_4I} + \underset{\text{Potassium Sulphate.}}{K_2SO_4.}$$

The mixture is then thrown into a funnel, previously stopped with cotton, allowed to drain, and the residual potassium sulphate washed with a mixture of 2 volumes of water and 1 volume of alcohol. The filtrate containing the ammonium iodide is then evaporated carefully to dryness, stirring, in order to granulate the salt.

When prepared according to this process ammonium iodide always contains small quantities of ammonium sulphate. The product should be kept in small, well-stopped vials protected from the light.

Properties.—Ammonium iodide occurs in minute, colorless, cubical crystals, odorless, and having a sharp, saline taste. It is soluble at 15° in 1 part of water and in 9 parts of alcohol, in 0.5 part of boiling water and in 3.7 parts of boiling alcohol. When heated, it evolves vapors of iodine and completely volatilizes without melting. Its aqueous solution is neutral to litmus paper.

Ammonium iodide deliquesces when exposed to the air, and gradually decomposes with a yellow color, due to the liberation of free iodine. The colored salt has a faint odor of iodine. It

should not be decomposed when colored, but may be reclaimed by dissolving in water, decolorizing with a small quantity of ammonia water, evaporating and granulating.

AMMONIUM AND SULPHUR.

Ammonium Monosulphide $(NH_4)_2S$.—When 2 volumes of ammonia gas and 1 volume of hydrogen sulphide are mixed at a temperature of —18°, ammonium monosulphide is formed. It forms colorless, glittering crystals, which commence to decompose at ordinary temperatures into ammonia and ammonic sulphydrate. This compound is prepared in aqueous solution by saturating 3 parts of solution of ammonia with hydrogen sulphide and then adding 2 parts of ammonia water. This is the official test-solution. It is a valuable reagent in the laboratory, and is very extensively used.

Ammonium Hydrosulphide, NH_4SH.—This compound is obtained when ammonia gas and hydrogen sulphide are mixed at ordinary temperatures; on cooling to o°, colorless, acicular crystals separate. These crystals are formed when alcoholic ammonia is saturated with hydrogen sulphide. The compound is formed in aqueous solution when aqueous ammonia is saturated with hydrogen sulphide:

$$NH_4OH + H_2S = NH_4SH + H_2O.$$

This solution and the preceding one of ammonium monosulphide are colored yellow on standing, owing to the formation of the higher ammonium polysulphides and water. There are at least three of these higher sulphides: *ammonium tetrasulphide*, $(NH_4)_2S_4$, obtained by cooling the mother liquor from the pentasulphide and saturating it with ammonia and hydrogen sulphide; *ammonium pentasulphide*, $(NH_4)_2S_5$, prepared by dissolving sulphur in the solution of hydrosulphide; and *ammonium heptasulphide*, $(NH_4)_2S_7$, formed when the pentasulphide is exposed to the air.

OXYGEN SALTS OF AMMONIUM.

Ammonium Sulphate, $(NH_4)_2SO_4$.—This salt is met with as a by-product in the manufacture of boric acid, and is found native as the mineral *mascagnite*. It is prepared by saturating ammoniacal gas-liquor with sulphuric acid, evaporating rapidly, and removing the crystals as they form by perforated ladles. As thus obtained the crystals are of a dark color. They are first allowed to drain well, then dissolved in water, treated with animal charcoal, filtered, and recrystallized.

Properties.—Ammonium sulphate occurs in large, transparent, rhombic crystals, isomorphous with potassium sulphate. They are soluble in 1.3 parts of water at 15°, and in 1 part of boiling water, insoluble in absolute alcohol, but slightly soluble in ordinary alcohol. On the application of heat the crystals melt

at 140° ; at 280° they decompose, with evolution of ammonia, water, and nitrogen ; at the same time ammonium sulphite with some sulphate sublimes.

Uses.—Ammonium sulphate is one of the most useful of the ammonium salts, since it forms the easiest method of recovering the ammonia from gas-liquors, and it is then used as a basis for the preparation of the other ammonium salts. It is especially employed in the manufacture of ammonia-alum and as a fertilizer.

Acid Ammonium Sulphate, NH_4HSO_4, is obtained when the neutral sulphate is crystallized in dilute sulphuric acid.

It forms rhombic crystals which resemble in form those of acid potassium sulphate.

Ammonium Nitrate, NH_4NO_3.—The usual process for obtaining this salt is by saturating nitric acid with ammonium hydrate or carbonate ; a somewhat more economical method consists in mixing solutions of ammonium sulphate and potassium nitrate; the result is double decomposition with the formation of potassium sulphate and ammonium nitrate ; the latter, being much more soluble, is obtained after the potassium sulphate has crystallized out.

Properties.—Ammonium nitrate is found in commerce in long, thin, colorless, rhombic prisms, or in white, fused masses, or as a white, granular powder ; it is odorless, has a sharp, bitter, saline taste, and is somewhat deliquescent. Its aqueous solution is neutral to litmus paper. The salt is soluble at 15° in 0.5 part of water and in 20 parts of alcohol ; it is very soluble in boiling water and in 3 parts of boiling alcohol. It melts at 165°, and between 230° and 250° it is decomposed into nitrogen monoxide and water, as follows :

$$NH_4NO_3 = N_2O + 2H_2O.$$

A small proportion of the salt is sublimed unchanged at the same time. The fused salt acts as an energetic oxidizing agent.

Uses.—Ammonium nitrate is used largely in the production of nitrogen monoxide, or laughing gas. The salt when dissolved in water produces a decided fall in temperature.

Ammonium Nitrite, NH_4NO_2, is formed by decomposing a solution of silver nitrite with ammonium chloride :

$$NH_4Cl + AgNO_2 = NH_4NO_2 + AgCl.$$

The crystals are obtained from this by evaporating the filtrate at ordinary

temperatures over sulphuric acid. Ammonium nitrite occurs in indistinctly crystalline masses, which decompose when heated into water and nitrogen.

Normal Ammonium Phosphate, $(NH_4)_3PO_4.3H_2O$, is sometimes found in guano; it is also obtained by mixing a concentrated solution of hydrogen diammonium phosphate with water of ammonia. There are deposited small prismatic or acicular crystals, which decompose when exposed to the air, or when the solution is boiled.

Hydrogen Diammonium Phosphate, $(NH_4)_2HPO_4$, is also found in some guanos, and is prepared by evaporating a solution of phosphoric acid with a slight excess of ammonia. The salt is deposited in transparent monoclinic prisms.

Dihydrogen Ammonium Phosphate, $NH_4H_2PO_4$.—When the phosphoric acid is in slight excess with ammonia, crystals of this compound separate out.

Hydrogen Ammonium Sodium Phosphate, $NaNH_4HPO_4.4H_2O$.—Microcosmic salt occurs in guano and in putrid urine. The salt is prepared by dissolving 5 parts of ordinary sodium phosphate, $Na_2HPO_4.12H_2O$, in hot water, adding to a hot solution of the ordinary ammonium phosphate, $(NH_4)_2HPO_4$, and allowing the solution to cool. The salt separates in transparent, monoclinic, prismatic crystals. They have a distinctly saline taste, and are readily soluble in water. On the application of heat the salt melts, gives off water and ammonia, and leaves a residue of the dihydrogen sodium phosphate; the further application of heat melts this salt to clear liquid with further loss of water, and with the formation of sodium hexametaphosphate, which forms a clear glass on cooling. Because of this property of forming a clear glass the salt is largely used in blowpipe analysis.

Ammonium Carbonate, $NH_4HCO_3.NH_4NH_2CO_2$. **Ammonii Carbonas, U. S.** P.—As will be seen from the above formula, the official salt is a compound of the acid ammonium carbonate with ammonium carbamate. Normal ammonium carbonate, $(NH_4)_2CO_3$, is obtained when the official salt is dissolved in water:

$NH_4HCO_3.NH_4NH_2CO_2$	+	H_2O	=	NH_4HCO_3	+	$(NH_4)_2CO_3$.
Official Ammonium Carbonate.		Water.		Acid Ammonium Carbonate.		Normal Ammonium Carbonate.

When the normal carbonate is desired in quantity and in a solid form, the official compound is digested for 2 hours at a temperature of 12° with strong aqueous ammonia; the resulting white, crystalline powder is dried by pressing between folds of absorbent paper. These crystals are readily converted into the acid carbonate.

The official, which is also the commercial, salt is prepared by heating in iron retorts ammonium sulphate and calcium carbonate or chalk, with sometimes a small quantity of charcoal:

$$2(NH_4)_2SO_4 + 2CaCO_3 = NH_4HCO_3.NH_4NH_2CO_2 + NH_3 + H_2O + 2CaSO_4.$$

Ammonium Sulphate. | Calcium Carbonate. | Official Ammonium Carbonate. | Ammonia. | Water. | Calcium Sulphate.

After the condensation of the ammonium carbonate, the uncondensed vapors, containing water and ammonia, are led into sulphuric acid in order to recover the ammonia.

Crude ammonium carbonate may also be prepared by passing ammonia, liberated from gas-liquors by lime, into leaden chambers along with carbon dioxide and water.

$$3NH_3 + 2CO_2 + H_2O = NH_4HCO_3.NH_4NH_2CO_2.$$

Ammonia. | Carbon Dioxide. | Water. | Official Ammonium Carbonate.

Properties.—The official ammonium carbonate occurs in "white, hard, translucent, striated masses, having a strongly ammoniacal odor without empyreuma, and a sharp, saline taste. On exposure to the air, the salt loses both ammonia and carbonic acid, becoming opaque, and is finally converted into friable, porous lumps, or a white powder." The salt is soluble in about 5 parts of water at 15°; it is decomposed by boiling water, with the elimination of carbonic acid and ammonia, resulting finally, after prolonged boiling, in complete dissipation of the salt. Alcohol dissolves the carbonate, leaving the acid carbonate behind. On the application of heat, ammonium carbonate is completely dissipated without darkening or charring. The aqueous solution reacts alkaline to litmus, and effervesces strongly with acids.

Hydrogen Ammonium Carbonate, NH_4HCO_3. Ammonium Bicarbonate.—Crystals of this salt have been found in Patagonian guano and in the purifiers of gas-works.

When the commercial carbonate is exposed to the air for some time a white powder results, consisting of the bicarbonate; it may also be prepared by passing carbon dioxide into an aqueous solution of the ordinary carbonate. It is usually found as a white, mealy powder, but may be obtained in large rhombic crystals by allowing them to form slowly from aqueous solution. At 60° it is slowly decomposed into ammonia, water, and carbon dioxide. The salt is soluble in 8 parts of water at 15°; it is insoluble in alcohol.

LITHIUM.

Symbol, Li. *Atomic Weight*, 7.01. *Valence*, I.

History.—In 1817, Arfvedson, while working in the laboratory of Berzelius, found a peculiar substance in the mineral *petalite* from the Swedish iron-mines at Utö. The metal was first isolated by Bunsen and Matthiessen in 1855.

Occurrence.—While lithium is not found in large quantities, it is still widely distributed in the three kingdoms. In the mineral kingdom it is found in *petalite*, a silicate of aluminum, sodium, and lithium, to the extent of 2.7 to 3.7 per cent.; in *lepidolite*, a lithia mica, 1.3 to 5.7 per cent.; and in *spodumene*, a silicate of aluminum, sodium, and lithium, 3.8 to 5.6 per cent. It is found in a number of mineral waters, the most notable in the United States being the springs at Gettysburg. In the vegetable kingdom, lithium has been detected in the ash of the vine, of seaweed, and of tobacco. The animal kingdom contains small quantities of this metal, as shown by its detection in the ashes of blood and milk and in muscular tissue.

Preparation.—In order to obtain metallic lithium, the chloride is first formed. This is accomplished by fusing at the highest temperature of a wind furnace 10 parts of finely-powdered lepidolite, 10 parts of barium carbonate, 5 parts of barium sulphate, and 3 parts of potassium sulphate. The heavy barium compounds settle to the bottom, while potassium and lithium sulphate remain at the top of the fused mass, and are extracted by water. The sulphates are converted into chlorides by the addition of barium chloride, the solution evaporated to dryness, and the lithium chloride separated from the potassium salt by solution in a mixture of absolute alcohol and ether.

The metal is obtained by fusing the chloride in a small porcelain crucible, and decomposing by an electric current from a zinc-carbon battery of from four to six cells. The positive pole is a small piece of gas carbon, while the negative pole is an iron wire the thickness of a knitting-needle. In a few minutes the metal collects around this wire, and when it has attained the size of a pea, and before it becomes so large as to rise to the surface, it is lifted out by a spoon-shaped iron spatula, and cooled under naphtha.

Properties.—Lithium possesses the silver-white lustre of sodium and potassium, but does not tarnish by oxidation so easily as they do. It is the lightest of all known solids, having a specific gravity, according to Bunsen, of 0.5891 to 0.5983. It floats on ordinary petroleum, and can only be preserved under the lightest gasoline.

When heated to 180° lithium melts, and at a higher temperature ignites, and burns with a brilliant red flame. In contact with water it does not oxidize so actively as sodium, as not sufficient heat is evolved to melt it. Most of the acids act on it slowly, but concentrated nitric acid attacks it with explosive violence.

COMPOUNDS OF LITHIUM.

Lithium Chloride, LiCl.—This salt is usually prepared by dissolving the carbonate in hydrochloric acid, or it is made directly from petalite as described under the metal. When the aqueous solution is evaporated slowly over sulphuric acid at ordinary temperatures, the salt is obtained in octohedra. It is very soluble in water, being one of the most deliquescent salts known. It is soluble in alcohol and in a mixture of absolute alcohol and ether. Lithium chloride fuses at a low red heat, and at a higher temperature is slowly volatilized. On evaporating its aqueous solution to dryness, the salt is slightly decomposed, hydrochloric acid being given off, and the residue becoming alkaline.

Lithium Bromide, LiBr. **Lithii Bromidum**, U. S. P.—This salt is obtained by neutralizing hydrobromic acid with lithium carbonate. It occurs as a white, granular, crystalline powder, odorless, and with a sharp, slightly bitter, saline taste, and a neutral reaction. It is soluble in 0.6 part of water at 15°, and in 0.3 part of boiling water, very soluble in alcohol, and soluble in ether. On the application of heat, lithium bromide melts at low redness, and at a higher temperature is slowly volatilized.

Lithium Oxide, Li_2O, is formed when the metal is burned in air. It is prepared by heating the nitrate to redness in a silver basin. It forms a white, crystalline mass, which dissolves in water with the formation of the hydrate, LiOH. The latter behaves in many respects like sodium hydrate, but is less energetic.

Normal Lithium Sulphate, $Li_2SO_4.H_2O$, is formed in the decomposition of petalite, or other lithia mineral, as described under the metal, or dilute sulphuric acid is neutralized with lithium carbonate. It crystallizes in thin monoclinic plates, and is easily soluble in water and in alcohol. The acid salt, $LiHSO_4$, is also known.

Double Potassium and Lithium Sulphate, $KLiSO_4$, is obtained by dissolving the molecular weight of each salt in water, mixing, and allowing to crystallize, when rhombic crystals of the double salt separate out.

Lithium Phosphate, Li_3PO_4, is quite insoluble in water, which gives it some analytical interest, since lithium salts are thereby separated from the other alkaline metals.

Normal Lithium Carbonate, Li_2CO_3. **Lithii Carbonas**, U. S. P.—On account of its sparing solubility in water, this salt differs from the carbonates of sodium and potassium. It rather forms a connecting link between this group of metals and the next, consisting of calcium, strontium, and barium, whose carbonates it resembles.

Lithium carbonate may be prepared by precipitation of a soluble salt, like the sulphate or chloride, with sodium or ammonium carbonate, and boiling. It is, however, prepared from its source, lepidolite, by powdering and heating the mineral and then digesting with sulphuric acid. The mass with the acid is gently heated, and the cooled product extracted with water. The aqueous solution is boiled with milk of lime, by which iron and aluminum are removed ; the filtrate from them consists of potassium, sodium, and lithium hydrates, with a small quantity of lime ; the latter is removed by evaporating to dryness and dissolving in a small quantity of hot water, by which a solution is obtained containing the hydrates of the alkalies ; from this the lithium carbonate is precipitated by boiling with ammonium carbonate.

This may be purified by suspending 1 part of the carbonate in 20 parts of water and effecting solution by saturating with carbon dioxide, which forms the bicarbonate, $LiHCO_3$; after filtering, the solution is boiled, whereby a pure salt is thrown down.

Properties.—Lithium carbonate is a light, white, odorless powder, with an alkaline taste and reaction. It is permanent in the air ; soluble in 80 parts of water at 15° and in 140 parts of boiling water, insoluble in alcohol. On the application of a temperature approaching redness, lithium carbonate melts, and gives off some carbon dioxide ; when this melted mass cools, it forms a crystalline mass of lithium carbonate and oxide. The carbonate is also somewhat decomposed when its aqueous solution is boiled for a long time, carbon dioxide escaping and lithium hydrate being formed.

Lithium Bicarbonate, $LiHCO_3$, is not known except in aqueous solution.

Uses.—The salts of lithium have come into use chiefly because of the power possessed by the carbonate of dissolving uric acid. The bromide is supposed to have some advantages over the other alkali bromides, because of the relatively smaller proportion of the base present.

RUBIDIUM.

Symbol, Rb. *Atomic Weight,* 85.2. *Valence,* I.

History.—Rubidium was discovered in 1861 by Bunsen and Kirchhoff, by means of the spectroscope.

Occurrence.—It is found in nature, usually along with potassium, in many mineral waters, chiefly those of Dürkheim, in Baden ; in some minerals, as *lepidolite* and *petalite ;* and in the ashes of some plants. It is widely distributed, but only in small quantity.

Preparation.—Bunsen recommended the saline residue, after the preparation of lithium from lepidolite, as a source for rubidium salts. The rubidium precipitate with platinum is more insoluble than that of potassium; the latter is separated, therefore, by repeated boiling of the mixed platinum precipitates with small quantities of water. The rubidium compound is reduced by hydrogen, when a chloride is obtained, which furnishes a starting-point for the other salts. The metal is obtained by the same process used in preparing potassium,—namely, by distillation of the charred tartrate.

Properties.—Rubidium is a silver-white metal, which has a waxy consistence as low as —10°. Its specific gravity is 1.52, and it melts at 38.5°. Below a red heat it gives off a bluish vapor. When exposed to the air it inflames spontaneously, and when thrown on water acts energetically, decomposing the latter, burning with a violet flame.

SALTS OF RUBIDIUM.

Many of these salts have been prepared, and found to closely resemble those of potassium, with which they are isomorphous.

Their behavior in the colorless flame is very similar to that of potassium, the flame being a trifle redder. The flame spectrum exhibits two characteristic lines in the violet, which forms the most certain means of detecting rubidium salts. Bunsen stated that he could detect 0.002 milligramme by this reaction.

CÆSIUM.

Symbol, Cs. *Atomic Weight*, 132.7. *Valence*, I.

History.—Cæsium, like rubidium, was discovered by Bunsen and Kirchhoff by means of the spectroscope. This occurred in 1860.

Occurrence.—Cæsium is widely distributed in nature, but in small quantity, the largest quantity being in the mineral *pollux*, found in the island of Elba; it was found to contain 32 per cent. of cæsium; this mineral has also been found at Hebron, Maine, under the name of *pollucite*.

Cæsium is also found in many mineral springs, but not in the ashes of plants, as it is claimed that, in the absence of potassium compounds, cæsium acts as a poison towards plant life.

Preparation.—Cæsium does not appear to be so easily prepared as rubidium. Electrolysis of its cyanide has been attended with some success. Fusion of the hydrate with metallic aluminum has been attended with better results.

Properties.—Cæsium is a silver-white, very soft metal, melting at 26.5°, and having a specific gravity of 1.88. It inflames on exposure to the air, and is the most electro-positive metal known.

SALTS OF CÆSIUM.

The salts of this metal closely resemble those of rubidium and potassium. They color the flame still more reddish, form a double salt with platinum, and react similarly with other reagents. The metal was discovered by its characteristic spectrum, which consists of two intense blue lines and one less intense orange-red line.

CHAPTER II.

THE ALKALINE EARTH GROUP.

The alkaline earth metals are **Calcium, Strontium,** and **Barium**; they resemble the alkalies in part, and still bear some resemblance to the earths like alumina. The hydrates of this group resemble those of the alkalies, although not so soluble in water, but the carbonates, sulphates, and phosphates, unlike those salts of the alkalies, are insoluble in water.

The metals of the alkaline earths possess a distinct lustre and a white or golden-yellow color. They do not change so rapidly when exposed to the air as the metals of the alkali group. The oxides of these metals are white in color, and possess many properties peculiar to the earths. They are not affected by high temperatures, and are not reduced by hydrogen or carbon under these circumstances. The metals are heavier than water, and decompose it at ordinary temperatures, but not so energetically as the alkali metals.

CALCIUM.

Symbol, Ca. *Atomic Weight,* 39.91. *Valence,* II.

History.—The use of lime in mortar for building purposes by the ancients indicates that this substance was well known to them. A description of the process of lime-burning is found in the writings of Dioscorides and of Pliny. Lime and many of its compounds were designated *earths* by the ancients, and not distinguished from many other substances possessing this generic name. Towards the middle of the eighteenth century it was found that different kinds of earths existed, and lime was recognized as a distinct kind of earth.

The metal was first obtained by Davy, in 1808, by the electrolysis of calcium chloride in the presence of mercury; an amalgam of calcium and mercury resulted, which, when heated, gave off mercury, and left the calcium as a powder. In 1856, Bunsen and Matthiessen obtained larger quantities by the electrolysis of the fused chloride.

Occurrence.—The compounds of calcium are widely distributed in nature, the carbonate being the most abundant. The latter is found as calc-spar, arragonite, chalk, marble, and lime-

stone, in a comparatively pure condition, but many other minerals contain the carbonate as one of the constituents. The most abundant of these is dolomite, a magnesian limestone, which frequently forms whole mountain ranges.

Calcium fluoride or fluor-spar, CaF_2, is found in considerable quantities throughout the globe; the chloride, $CaCl_2$, occurs in sea water and in many mineral springs. The sulphate is found in the anhydrous condition as anhydrite, $CaSO_4$, or in the hydrated form as selenite or gypsum, $CaSO_4.2H_2O$. The phosphate is found, with chloride or fluoride, in apatite and osteolite. Nearly all silicates contain a considerable proportion of calcium. Calcium in some form is a constituent of all plants and animals. If deprived of it they die, since they will admit of the replacement of other elements, like magnesium, to a limited extent only.

Calcium has also been detected in meteorites, in the sun, and in some fixed stars.

Preparation.—The metal calcium is prepared by electrolysis of the fused chloride, or it may be obtained by heating in a closed iron crucible 1 part of sodium with 7 parts of fused calcium iodide. The temperature is first raised to a dull red heat and then to bright redness. It has also been prepared by strongly heating a mixture of 3 parts of calcium chloride, 4 parts of zinc, and 1 part of sodium; an alloy of zinc and calcium results, which is heated in a crucible made of gas-carbon until the zinc volatilizes; the calcium remains in the form of a button.

Properties.—Calcium is a yellow, lustrous, tough, and malleable metal. It is about as hard as gold, and has the specific gravity 1.5778. It does not oxidize readily in dry air, but in moist air it quickly becomes covered with the hydrate, the action gradually extending through the whole mass. Water is decomposed by calcium at ordinary temperatures with violent evolution of hydrogen; the heat developed, however, is not sufficient to inflame the latter. On the application of heat, calcium burns in the air with a very brilliant yellow flame. Dilute nitric acid dissolves the metal with such energy that the latter sometimes inflames, but concentrated nitric acid does not attack it until the temperature is raised to the boiling point of the acid.

CALCIUM AND THE HALOGENS.

Calcium Chloride, $CaCl_2$. **Calcii Chloridum, U. S. P.**—This salt was first prepared by Isaac Hollendus, in the fourteenth century, who designated it by the title *sal ammoniacum fixum*, be-

cause he prepared it by heating a mixture of sal ammoniac and lime.

It is found in sea water and in many mineral waters; it also occurs as tachydrite at Stassfurt; this is a compound with magnesium chloride, having the formula $CaCl_2, 2MgCl_2.12H_2O$.

Preparation.—Crude calcium chloride is a by-product in several chemical operations; for example, it is the residue in the preparation of ammonia from ammonium chloride; it is obtained in the preparation of potassium chlorate, in the ammonia-soda process, and in the preparation of carbon dioxide from limestone and hydrochloric acid. For many uses this crude product, which is in aqueous solution, is evaporated to dryness in an iron kettle, and then heated until it melts. The product is sent into commerce for dehydrating purposes as fused calcium chloride.

Purified calcium chloride is made by nearly saturating hydrochloric acid with marble, adding chlorine water to oxidize the iron and manganese compounds, and precipitating these by the addition of a slight excess of milk of lime (calcium hydrate). The clear, filtered solution, which is slightly alkaline, is carefully neutralized with hydrochloric acid. This solution is then evaporated to the crystallizing point or to dryness, according to the uses to which it is to be applied.

Properties.—The crystallized salt occurs in large, hexagonal prisms, having the composition $CaCl_2.6H_2O$. On the application of heat it melts at 29°. These crystals rapidly deliquesce on exposure to the air, forming a thick, oily liquid, formerly known as *oleum calcis*.

When the crystals dissolve in water a considerable fall in temperature takes place. A temperature of —48° is obtained by mixing $1\frac{1}{3}$ parts of the crystals with 1 part of snow. When heated to 200°, or when kept for some time over concentrated sulphuric acid, the crystals lose 4 molecules of water of crystallization, a white powder resulting, which possesses energetic dehydrating properties. Above 200° the remaining 2 molecules of water are driven off, and at 720° the salt becomes anhydrous.

The official salt is directed to be "calcium chloride, rendered anhydrous by fusion at the lowest possible temperature." It is described as occurring in "white, slightly translucent, hard fragments, odorless, having a sharp, saline taste, and very deliquescent."

The anhydrous salt is soluble in 1.5 parts of water, and in 8 parts of alcohol at 15°, in 1.5 parts of boiling alcohol, and very

freely soluble in boiling water; it is insoluble in ether. Since the aqueous solution is used for maintaining a temperature above that of boiling water, it is useful to know the boiling point of such a solution; that containing 50 parts of the anhydrous salt in 100 of water boils at 112°, that containing 200 per cent. of the salt boils at 158°, and that containing 325 per cent. boils at 180°.

The pure salt dissolves in water without residue, and has a neutral reaction. If, however, it be kept at or above the fusing point for some time, a slight decomposition takes place, so that it leaves a residue insoluble in water, and the solution has a faintly alkaline reaction.

Uses.—Calcium chloride has some use in the laboratory as a reagent, but its chief value is as a desiccating agent, in the drying of gases, and in the concentration of liquids. Its solution is valuable, as above stated, for use in water-baths, where it is desired to maintain a constant temperature above that of boiling water.

Calcium Bromide, $CaBr_2$. **Calcii Bromidum, U. S. P.**—Like the preceding salt, calcium bromide is found in certain mineral waters.

It is prepared by neutralizing hydrobromic acid with marble, adding bromine water to oxidize iron and manganese compounds, and precipitating these by the addition of a slight excess of milk of lime. The solution is filtered, and the filtrate carefully neutralized with hydrobromic acid. The resulting solution is then evaporated to dryness and carefully heated to 680°, whereby an anhydrous salt is obtained.

The Pharmacopœia directs that the anhydrous salt be employed. In this state it occurs as white, granular, very deliquescent salt, without odor, and with a sharp, saline taste. At 15° it is soluble in 0.7 part of water, and in 1 part of alcohol; at the boiling point these liquids dissolve it freely. At 680° the salt melts, above that temperature it is slowly decomposed with loss of bromine. The aqueous solution is neutral to litmus paper.

Uses.—The principal use of this salt is in medicine. It is supposed to have some advantages over the other bromides.

Calcium Iodide, CaI_2, is prepared like the bromide, which it resembles in many particulars. Both salts are so extremely deliquescent that considerable care is necessary in order to keep them in the solid state.

Calcium Fluoride, CaF_2, under the name of fluor-spar, occurs quite abundantly in nature. It is found especially in the limestone caves of the Castleton Valley in Derbyshire, England; considerable quantities are

also found in Saxony. It occurs in cubes and octohedra, and in some other forms belonging to the regular system.

It is also found in the ashes of some plants, in bones, in the enamel of the teeth, and in sea water and mineral springs.

In the pure condition calcium fluoride is colorless, but it is much oftener of a violet, blue, red, green, or brown color, owing to the presence of small quantities of impurities. At a red heat calcium fluoride fuses without decomposition; while hot it phosphoresces in the dark.

Fluor-spar is extensively employed as a flux in many metallurgical operations, and the finer masses of crystals are made into vases and other ornaments.

CALCIUM AND OXYGEN.

Calcium Monoxide, CaO. **Calx**, U.S.P.—Lime is prepared by heating calcium carbonate. If a pure carbonate is used a correspondingly pure product results. In a small way this is accomplished by heating calc-spar or a pure marble in a crucible with a hole in the bottom in order that the furnace gases may pass through and carry off the carbon dioxide.

$$\underset{\text{Calcium Carbonate.}}{CaCO_3} = \underset{\text{Calcium Oxide.}}{CaO} + \underset{\text{Carbon Dioxide.}}{CO_2}.$$

On a commercial scale lime-kilns are used. These were formerly constructed so as to be filled with limestone and fuel in alternate layers. Fire was then started at the bottom, and the temperature regulated by the air-supply below. Such a furnace, however, could only be emptied when cool. At the present time continuous furnaces are much more used. Such a one is shown in Fig. 120. It is built on the slope of a hill, so as to bring the door at the top on a level with the ground to facilitate the introduction of the limestone. The heat is supplied by two fires, F, F, the finished product is removed at D, Fig. 121. Fig. 120 shows a section cut parallel with the side of the hill, while Fig. 121 shows a section cut at right angles to this, by which the draw-hole D is shown. These furnaces are used in the well-known lime districts of Chester Valley, near Philadelphia. At the ordinary pressure of the atmosphere, a temperature of 812° is required for the dissociation of limestone, but in practice a temperature of 925° is usually employed. If the limestone contain much magnesia it is liable to sinter and form a semi-fused mass, so that in burning this variety a lower heat must be maintained. Coal is the chief fuel used at the present time, although formerly much wood was employed.

Properties.—Pure lime occurs in white, amorphous masses. It often contains iron, and consequently is of a grayish or yellowish shade of color. When exposed to the air it gradually absorbs moisture and carbon dioxide, and crumbles to a white powder. Lime is without odor, but has a sharp, caustic taste. It is soluble in about 750 parts of water at the ordinary temperatures, and in 1300 parts of boiling water; insoluble in alcohol. It is not affected by the highest degrees of heat, but the oxyhydrogen flame causes it to emit an intense white light.

When lime is treated with about one-third its weight of water, added drop by drop, it gradually becomes hot, swells to about twice its bulk, and then falls to a white powder.

The solubility and some of the other properties of lime are closely associated or iden-

FIG. 120.

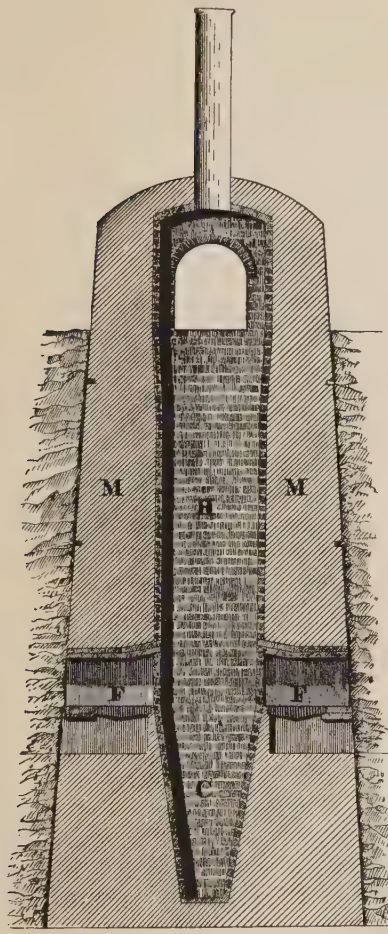
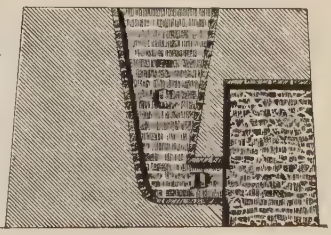


FIG. 121.



Lime-kiln.

tical with those of calcium hydrate, since, in the presence of water, the oxide is first converted into hydrate.

Calcium Hydrate, $Ca(OH)_2$, *Calcium Hydroxide.*—When lime is treated with one-third its weight of water, as stated above, the product is calcium hydrate. Considerable heat is developed in

this operation where the proportions are carefully adjusted a temperature of 150° is easily attained. The reaction involved in the formation of the hydrate is as follows:

$$CaO + H_2O = Ca(OH)_2.$$

The resulting product is a fine, white, impalpable powder. Its solution in water forms **Liquor Calcis**, U. S. P., or lime water. This solution has a saline and somewhat caustic taste and an alkaline reaction. On boiling it becomes turbid, owing to the lesser solubility of the hydrate in hot than in cold water. When the clear solution is exposed to the air, a pellicle forms on the surface, due to the formation of calcium carbonate, resulting from the absorption of carbon dioxide from the atmosphere. Calcium hydrate may be obtained by adding sodium or potassium hydrate to a concentrated solution of calcium chloride.

Crystals of calcium hydrate, in the form of tablets or small prisms, may be obtained by evaporating the clear solution of lime water in a vacuum over sulphuric acid.

Milk of lime is a mixture of calcium hydrate and water. It may be made of any desired strength by agitating the freshly-slaked lime with water.

Uses.—Calcium oxide, and therefore also the hydrate, is largely used as a laboratory reagent. The oxide finds much use as a desiccating agent for gases. The hydrate is considerably employed in medicine. The hydrate is largely used in the manufacture of mortar.

Mortars and Cements.—When freshly slaked lime of the consistence of paste is mixed with an equal volume of water, and then 3 to 4 times as much sand is added as there was lime employed, the result is mortar.

The process of hardening which mortar undergoes is called "setting." This setting is sufficiently complete in a few days to give stability to a structure in which it is employed, but the hardening process continues for years. The peculiar action of mortar appears to be due to loss of water and subsequent absorption of carbon dioxide, rather than to the formation of calcium silicate. The value of a mortar depends to a great degree upon the thorough mixing of the ingredients in the process of manufacture. The nature of hydraulic cements will be explained under "Clays" in the section on alumina.

Calcium Dioxide, CaO_2, is prepared by precipitating lime water with hydrogen dioxide. This precipitate has the composition $CaO_2.8H_2O$:

it is crystalline, the crystals being in quadratic tables or prisms; they are almost insoluble in water and insoluble in alcohol. The crystals effloresce when exposed to the air, and at 130° lose all their water, becoming anhydrous; at higher temperatures they give off half of their oxygen without undergoing fusion.

OXYGEN SALTS OF CALCIUM AND THE HALOGENS.

Calcium Hypochlorite, $Ca(OCl)_2$, is prepared in a state of purity with great difficulty; a commercial preparation in which it enters is well known, however, as **Calx Chlorata**, U. S. P., or *chlorinated lime*, *chloride of lime*, *bleaching powder*, *bleach*, etc.

Chlorinated lime was first prepared on a commercial scale by Tennant, of Glasgow, in 1798. By some it is considered to be calcium chloro-hypochlorite, having the formula $Ca(OCl)Cl$, by others it is thought to be a mixture of calcium hypochlorite with calcium chloride, having the formula $Ca(ClO)_2CaCl_2.2H_2O$, and containing variable quantities of calcium hydrate. The former view, first proposed by Odling, seems to have been most generally adopted.

Preparation.—This important substance is prepared in enormous quantities in conjunction with alkali works. The chlorine is derived from the waste hydrochloric acid of the Leblanc process, or from the decomposition of magnesium chloride by steam in the ammonia-soda process (see pages 195 to 197). The lime is a finely powdered and sifted dry calcium hydrate. It is placed in chambers of stone, or iron covered with asphalt, to the depth of 4 or 5 inches. The chambers are usually 60 feet long, 18 feet wide, and 7 feet high. They are filled with chlorine and allowed to remain closed for about two days, when the gas is absorbed, and they are opened and the powder is turned. Chlorine is again run in and allowed to remain for another period of two days, when it is usually found that the lime contains from 36 to 37 per cent. of available chlorine. Occasionally a third absorption is resorted to, but this is not often necessary, except in hot weather, when the reaction is less rapid. Usually a series of these chambers are located near together so that the excess of chlorine may be passed from one to the other. In some other cases a series of shelves are arranged in a single chamber, and the contents of each shelf are removed as saturation is completed.

The reaction involved in the production of bleaching powder is considered to be as follows:

$$\underset{\text{Calcium Hydrate.}}{Ca(OH)_2} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Calcium Chloro-hypochlorite.}}{CaOCl_2} + \underset{\text{Water.}}{H_2O.}$$

Properties.—Chlorinated lime is officially described as "a white, or grayish-white, granular powder, exhaling the odor of hypochlorous acid, having a repulsive, saline taste, and becoming moist and gradually decomposing on exposure to air."

It is only partly dissolved by water or alcohol ; the aqueous solution first colors red litmus paper blue, and then bleaches it. It is decomposed by weak acids with evolution of chlorine, and at elevated temperatures dry carbon dioxide will decompose it.

The Pharmacopœia requires that chlorinated lime shall contain not less than 35 per cent. of available chlorine. Much of it comes in commerce packed in sealed paper boxes, coated on the inside with a water-proof material, so that the powder maintains its original strength satisfactorily until opened. In moist air it rapidly deteriorates when exposed.

Calcium hypochlorite may be obtained in crystals by allowing an aqueous solution of chlorinated lime to evaporate in a vacuum over sulphuric acid ; these have the composition $Ca(OCl)_2.4H_2O$, and very readily decompose. The fact that the hypochlorite is present in aqueous solution is explained by the supposition that calcium chloro-hypochlorite is decomposed by water as follows :

$$\underset{\text{Calcium Chloro-hypochlorite.}}{2CaOCl_2} = \underset{\text{Calcium Chloride.}}{CaCl_2} + \underset{\text{Calcium Hypochlorite.}}{Ca(OCl)_2.}$$

The chloro-hypochlorite is acted on by acids with the production of chlorine according to the following :

$$\underset{\text{Calcium Chloro-hypochlorite.}}{CaOCl_2} + \underset{\text{Sulphuric Acid.}}{H_2SO_4} = \underset{\text{Calcium Sulphate.}}{CaSO_4} + \underset{\text{Water.}}{H_2O} + \underset{\text{Chlorine.}}{Cl_2.}$$

On this last reaction depends the value of chlorinated lime in the bleaching industry.

The process of bleaching by free chlorine is one of oxidation ; it combines with hydrogen to form hydrochloric acid, while the liberated oxygen in the nascent state readily attacks coloring matters, water and a colorless compound resulting.

Uses.—Chlorinated lime is used most extensively for bleaching purposes ; it is very largely employed as a disinfecting agent, and is undoubtedly one of the best substances for this purpose. Where chlorine is desired in the free state chlorinated lime forms one of the most convenient and economical means of obtaining it,

the simple addition of a dilute acid being sufficient to produce it in liberal quantity, according to a reaction given above.

Calcium Chlorate, $Ca(ClO_3)_2$, is prepared by passing chlorine into hot milk of lime, or solutions of calcium silicofluoride and potassium chlorate are mixed, when potassium silicofluoride crystallizes out, leaving the calcium chlorate in solution, and the latter is crystallized from the very concentrated solution. Calcium chlorate is a very deliquescent salt, and is crystallized with considerable difficulty. The crystals contain 2 molecules of water of crystallization.

Calcium Bromate, $Ca(BrO_3)_2.H_2O$, and *Calcium Iodate*, $Ca(IO_3)_2.6H_2O$, are also known.

CALCIUM AND SULPHUR.

Calcium Monosulphide, CaS.—In 1750 Marggraf noticed that this substance had the property of remaining luminous in the dark after it had been exposed to bright light. It is obtained by heating calcium sulphate with powdered charcoal, or it may be prepared by leading the vapor of carbon disulphide and carbon dioxide over incandescent lime.

Calx Sulphurata, U. S. P. (Sulphurated Lime), is a crude calcium sulphide, prepared by taking 70 parts of dried calcium sulphate, 10 parts of charcoal, and 2 parts of starch. The ingredients are mixed thoroughly, packed in a loosely covered crucible, and heated to bright redness until the mass loses its black color. After the crucible cools the product should be reduced to a fine powder, and at once transferred to small, glass-stoppered vials.

The pure calcium sulphide occurs in white masses. The official product is described as "a pale gray powder, exhaling a faint odor of hydrogen sulphide, having a nauseous, alkaline taste, and gradually decomposed by exposure to air. Very slightly soluble in cold water, more readily in boiling water, which partially decomposes it; insoluble in alcohol."

Sulphurated lime is decomposed by dilute acids with evolution of hydrogen sulphide, even acetic acid being sufficiently strong to effect this change.

It has the property of being phosphorescent in the dark, giving out a greenish, bluish, or violet light, according to the method by which it was prepared.

It has some use in medicine, and may be employed to furnish arsenic-free hydrogen sulphide.

Calcium Sulphydrate, $Ca(SH)_2$, is prepared by saturating milk of lime with hydrogen sulphide:

$$\underset{\text{Calcium Hydrate.}}{Ca(OH)_2} + \underset{\text{Hydrogen Sulphide.}}{2H_2S} = \underset{\text{Calcium Sulphydrate.}}{Ca(SH)_2} + \underset{\text{Water.}}{2H_2O.}$$

It is known only in solution, and is employed as a depilatory.

Calcium Disulphide, CaS_2, is obtained in yellow crystals when milk of lime is boiled with an excess of sulphur, and the filtered solution allowed to cool. These crystals contain 3 molecules of water of crystallization.

OXYGEN SALTS OF CALCIUM AND SULPHUR.

Calcium Sulphite, $CaSO_3$, is precipitated when solutions of calcium chloride and sodium sulphite are mixed. It occurs as a white powder, soluble in 800 parts of cold water. This salt is obtained in crystals by allowing its solution in sulphurous acid to stand exposed to the air; they have the composition $CaSO_3.2H_2O$. A solution of this salt in excess of sulphurous acid is found in commerce under the name of *bisulphite of lime;* it is made by passing sulphur dioxide into milk of lime. It has extensive use as a preservative agent, especially among brewers. Calcium sulphite is employed as a preservative by cider-makers.

Calcium Sulphate, $CaSO_4$, *Gypsum.*—This compound was known to the ancients as a chalk-like substance; likewise the property which the dried gypsum possesses of hardening when moistened with water. Marggraf determined its composition in 1780.

Calcium sulphate is found native as anhydrite associated with limestone, or crystallized with 2 molecules of water as selenite. Two other varieties of this compound are known as satin spar or fibrous gypsum, and crystalline gypsum or alabaster.

This salt may be prepared by treating calcium carbonate, marble, or limestone with sulphuric acid; it is, however, rarely manufactured in this way, because of the abundance of it native, and because it is a by-product in so many chemical processes.

Calcii Sulphas Exsiccatus, U. S. P., is prepared by carefully drying the native gypsum until it loses three-fourths of its water; it then contains about 95 per cent. by weight of calcium sulphate and 5 per cent. of water. The native compound has a specific gravity of 2.31, and it may be deprived of its water at a temperature of 110°–120°. When thus dried it is commercially known as *burnt gypsum*, or *plaster of Paris.* If overheated—that is, above 200°—it will not take up water so readily, and will not harden.

Properties.—The official compound is described as "a fine, white powder, without odor or taste. From moist air it attracts water, becomes granular, and then loses the property of harden-

ing with water. When mixed with half its weight of water, Dried Calcium Sulphate forms a smooth, cohesive paste, which rapidly hardens. It is soluble in about 410 parts of water at 15°, in 388 parts at 38°, and in 476 parts at 100°. In alcohol it is insoluble. It readily dissolves in dilute nitric or hydrochloric acid, also in saturated solutions of potassium nitrate, sodium hyposulphite, and of various ammonium salts." When calcium sulphate is dissolved in hot hydrochloric or nitric acid and the solution is allowed to cool, it separates in glittering, silky, acicular crystals. On heating the salt with sulphuric acid to 100°, it is changed to a porous mass, of which a part dissolves and separates out again on cooling.

Uses.—Gypsum is used in large quantities as a fertilizer; it has some use as a cement, is employed somewhat in surgery, and is the material employed in making plaster casts and certain kinds of ornamental work. The artificially prepared salt, made by precipitating a concentrated solution of calcium chloride with dilute sulphuric acid, is used as a filling for writing-paper under the name of *pearl hardening* or *annaline*.

Calcium Potassium Sulphate, $CaSO_4K_2SO_4.H_2O$. — When intimate mixtures of equal weights of the anhydrous salts are stirred into less than their weight of water, the mass hardens almost immediately; by varying the proportion of water, different qualities of the solidified compound may be obtained. This mixture when used for plaster casts yields a material which possesses a polished surface.

Calcium Sodium Sulphate, $CaSO_4Na_2SO_4$, is found native as a mineral under the name of glauberite. The artificially prepared compound does not possess the same property of setting that the calcium and potassium compound does.

Calcium Thiosulphate, $CaS_2O_3.6H_2O$, is made by warming a mixture of calcium sulphate, sulphur, and water. It forms oblique, six-sided prisms, which are soluble in their own weight of water. The solution is decomposed at a temperature of 60°, sulphur separating.

OXYGEN SALTS OF CALCIUM AND NITROGEN.

Calcium Nitrate, $Ca(NO_3)_2$, occurs as an efflorescence on walls of stables and other places where organic matter is undergoing decomposition. It is abundant in some soils, especially that of nitre plantations.

Calcium nitrate is prepared by dissolving chalk or marble in nitric acid. The anhydrous compound is formed under ordinary circumstances, but when the aqueous solution is allowed to evaporate very slowly over sulphuric acid, crystals are formed con-

taining 4 molecules of water of crystallization. It is a very deliquescent salt, soluble in both water and alcohol. It is sometimes known as *lime saltpetre* or *wall saltpetre*. This salt was formerly used in the preparation of ordinary saltpetre, but has little use at the present time.

OXYGEN SALTS OF CALCIUM AND PHOSPHORUS.

Calcium Phosphate, $Ca_3(PO_4)_2$. **Calcii Phosphas, U. S. P.**—The salt of this formula is also known as *normal calcium orthophosphate* and *bone phosphate*. It is found native with calcium fluoride in the minerals apatite and phosphorite. The minerals osteolite and sombrerite are impure calcium phosphates. By far the most extensive occurrence of calcium phosphate is in what is known as the phosphate rock of South Carolina, Florida, and other parts of the Southern United States; it is also found in Canada. This rock frequently contains as much as 90 per cent. of calcium phosphate. Bones are largely composed of calcium phosphate; when burned, they contain from 80 to 85 per cent. of it.

Preparation.—Calcium phosphate is prepared by adding calcium chloride and ammonium hydrate to sodium phosphate:

$$\underset{\text{Calcium Chloride.}}{3CaCl_2} + \underset{\text{Ammonium Hydrate.}}{2NH_4OH} + \underset{\text{Sodium Phosphate.}}{2(Na_2HPO_4.12H_2O)} = \underset{\text{Calcium Phosphate.}}{Ca_3(PO_4)_2} + \underset{\text{Ammonium Chloride.}}{2NH_4Cl} + \underset{\text{Sodium Chloride.}}{4NaCl} + \underset{\text{Water.}}{26H_2O}.$$

Properties.—Calcium phosphate precipitates in the above reaction as a white, amorphous powder; it is odorless and tasteless, and permanent in the air. It is almost insoluble in cold water; decomposed by boiling water into an insoluble basic salt, and a soluble acid salt which dissolves. This reaction takes place very slowly in the presence of cold water, so that an exact determination of the solubility of calcium phosphate is impossible. It is readily soluble in solutions of ammonium salts, sodium nitrate, sodium chloride, and a number of other salts; solution of carbonic acid also has some solvent action upon it. At an intense white heat the salt fuses without decomposition.

Uses.—Calcium phosphate has some use in medicine, but that is insignificant compared with the extent and value of its application as a fertilizer. The phosphate industry commenced in South Carolina, in 1867, with the shipment of 6 tons; there are now

over half a million tons annually shipped from that State alone, while North Carolina and Florida produce sufficient to make the total shipments from the three States for 1893, 981,340 tons, valued at $3,434,690.

Dicalcium Orthophosphate, $Ca_2H_2(PO_4)_2$, or *Hydrogen Calcium Orthophosphate*, $CaHPO_4$.—This compound is precipitated when a solution of sodium phosphate is added to one of calcium chloride; it is a white, crystalline powder, containing 2 molecules of water of crystallization. Urinary concretions and deposits are made up largely of this phosphate.

Tetrahydrogen Calcium Phosphate, $CaH_4(PO_4)_2$, is prepared by dissolving either of the preceding phosphates in phosphoric acid and allowing the solution to evaporate spontaneously. This compound is also known sometimes as calcium superphosphate. What is commercially known as *superphosphate of lime* is a mixture of this compound and calcium sulphate, and is prepared by treating bones or phosphate rock with two-thirds of their weight of sulphuric acid. The product is extensively employed as a fertilizer.

Calcium Hypophosphite, $Ca(H_2PO_2)_2$. **Calcii Hypophosphis, U. S. P.**—This salt is prepared by taking 1 part of finely-divided phosphorus and 2 parts of calcium oxide which has been slaked with 1 part of water and then stirred with sufficient water to make a thin mixture.

These ingredients are mixed, placed in a well-ventilated position, and warmed to 40° until combination is complete, or until hydrogen phosphide ceases to be evolved:

$$\underset{\text{Calcium Hydrate.}}{3Ca(OH)_2} + \underset{\text{Phosphorus.}}{2P_4} + \underset{\text{Water.}}{6H_2O} = \underset{\text{Calcium Hypophosphite.}}{3Ca(H_2PO_2)_2} + \underset{\text{Hydrogen Phosphide.}}{2PH_3}.$$

When the reaction is ended the mixture is filtered and the calcium hydrate removed from the filtrate by carbon dioxide. It is again filtered, and the clear filtrate evaporated at a low temperature in a vacuum over sulphuric acid until crystallization takes place.

The finely-divided phosphorus is obtained by placing 1 part of phosphorus in a flask with 2 parts of powdered glass and 5 parts of water, applying a gentle heat until the phosphorus is melted, and then agitating until cold. By this means the phosphorus is obtained in small particles which more readily combine with the calcium hydrate. Instead of crystallizing the salt from its aqueous solution, it may be precipitated by the addition of alcohol.

Properties.—Calcium hypophosphite occurs in small, water-free, transparent, monoclinic prisms. It is also found in lustrous

scales, or in a fine, white powder. It is odorless, has a nauseous, bitter taste, and is permanent in the air.

The salt is soluble in 6.8 parts of water at 15° and in 6 parts of boiling water ; it is insoluble in alcohol.

On the application of heat calcium hypophosphite decrepitates, and above 300° it begins to decompose, giving off water, hydrogen, and hydrogen phosphide, and leaving a residue of calcium pyrophosphate and metaphosphate with some red phosphorus. The aqueous solution is neutral to litmus paper.

Uses.—Calcium hypophosphite has considerable use in medicine, and at the same time furnishes a convenient salt from which to prepare the other hypophosphites.

CALCIUM AND SILICA.

Calcium Silicate, $CaSiO_3$.—The compound of this formula occurs native as the mineral wollastonite; okenite, gyrolite, and xonotlite are polymeric compounds of this. Most natural silicates contain more or less calcium silicate. This compound may also be obtained by adding calcium chloride to a solution of sodium silicate, when it forms a gelatinous precipitate.

Calcium silicate enters into the composition of many varieties of glass.

CALCIUM AND CARBON.

Calcium Carbide, CaC_2.—This is an artificial compound prepared by melting a mixture of powdered lime and coke-dust in an electric furnace. It is a dark-brown, dense substance, having a crystalline metallic fracture of blue or brown appearance and a specific gravity of 2.26. It evolves a peculiar odor when exposed to the atmosphere, due to the action of atmospheric moisture. This odor is due to acetylene, which is always produced when calcium carbide is brought into contact with water or its vapor at ordinary temperatures :

$$\underset{\text{Calcium Carbide.}}{CaC_2} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Acetylene.}}{C_2H_2} + \underset{\text{Calcium Hydrate.}}{Ca(OH)_2}.$$

It also decomposes with snow at a temperature of —31° C. It is not acted upon by the vapor of water at high temperatures.

In a dry atmosphere it is odorless. When exposed to the air in lumps it becomes coated with a layer of calcium hydrate, which to a great extent protects the rest of the substance from further deterioration by atmospheric moisture. Calcium carbide is not inflammable, and can be exposed to the temperature of the ordinary blast-furnace without melting.

Calcium carbide is used as a source of acetylene for illuminating purposes. One pound of the pure material yields 5.9 cubic feet of that gas at 18° C.

OXYGEN SALTS OF CALCIUM AND CARBON.

Calcium Carbonate, $CaCO_3$. **Calcii Carbonas Precipitatus**, U. S. P.—In the form of chalk, limestone, and marble this compound occurs in nature so abundantly that whole mountain ranges are formed of it. It is also the chief constituent of egg-shells, of the shells of mollusks, and of coral. In chalk it is amorphous, in marble it is in crystalline masses, while in calcite and arragonite it occurs in distinct crystals. These two minerals illustrate its dimorphous character. Calcite, or calc-spar, has a specific gravity of 2.70 to 2.75, and crystallizes in hexagonal prisms, while arragonite has a specific gravity of 2.92 to 3.28, and occurs in the form of rhombic prisms. When carbon dioxide in small quantity is passed into cold lime water, the precipitate is at first amorphous, but soon becomes crystalline in the form of calc-spar; when, however, the lime water is hot, crystals of the arragonite form are deposited.

Preparation.—The official salt is prepared by adding a hot solution of sodium carbonate to one of calcium chloride:

Na_2CO_3	+	$CaCl_2$	=	$CaCO_3$	+	$2NaCl$.
Sodium Carbonate.		Calcium Chloride.		Calcium Carbonate.		Sodium Chloride.

The product is a fine, white powder, without odor or taste, and permanent in the air. It is almost entirely insoluble in water, 1 liter dissolving about 18 milligrammes. In the presence of ammonium hydrate or carbonate it is less soluble, but with the other ammonium salts its solubility is increased. Carbon dioxide also increases its solubility: a liter of water saturated with this gas will dissolve 70 milligrammes of the salt. This solubility is increased under pressure up to 3 grammes per liter, but not beyond this point. Such a solution when allowed to stand at ordinary temperatures deposits crystals having the composition $CaCO_3.5H_2O$.

Dilute acetic, hydrochloric, or nitric acid dissolves calcium carbonate with effervescence, leaving no residue.

On heating calcium carbonate to redness with access of air it parts with its carbon dioxide, leaving a residue of calcium oxide.

Creta Præparata, U.S.P., *Prepared Chalk*, is an amorphous

calcium carbonate prepared by the elutriation of chalk. The Pharmacopœia of 1870 gave a process for its preparation as follows :

"Take of Chalk, *a convenient quantity*. Add a little water to the Chalk and rub it into fine powder. Throw this into a large vessel nearly full of water, stir briskly, and, after a short interval, decant the supernatant liquor, while yet turbid, into another vessel. Treat the coarser particles of the Chalk, remaining in the first vessel, in a similar manner, and add the turbid liquid to that previously decanted. Lastly, set the liquor by, that the powder may subside, and, having poured off the water, dry the powder."

Prepared chalk is "a white, amorphous powder, often moulded into conical drops, odorless and tasteless ; permanent in the air." In other characters it is practically identical with the precipitated compound.

Uses.—Both of the above preparations are used in medicine; the prepared chalk is preferred by some of the manufacturers of tooth powders on account of its non-crystalline character.

Whiting and *Paris White* are commercial varieties of prepared chalk, not so carefully washed, and therefore not so white. They are used for polishing and for many other purposes where chalk is required in the arts.

STRONTIUM.

Symbol, Sr. *Atomic Weight*, 87.3. *Valence*, II.

History.—The mineral in which strontium was first detected was known as strontianite from its occurrence near the village of Strontian in Scotland ; and the metal takes its name from that source. The fact that this mineral contained a peculiar earth was first pointed out by Crawford in 1790. This was confirmed by Hope in 1792, and independently by Klaproth a year later. Davy in 1808 separated the metal in a pure state by electrolysis.

Occurrence.—Strontium is found in nature in the same combinations which characterize barium and calcium,—namely, as carbonate, $SrCO_3$, or strontianite, and as sulphate, $SrSO_4$, or celestine. Many calcium minerals also contain small quantities of strontium. Smaller amounts are found in sea water, in mineral waters, and in certain salt springs. It has also been found in the ashes of some sea plants, as *Fucus vesiculosus*.

Preparation.—Strontium is readily prepared by the electrolysis of the fused chloride, or by repeatedly heating a saturated solution of the fused chloride with an amalgam of 1 part sodium and 4 parts mercury to 90°. There results an amalgam of stron-

tium, which by drying between folds of filter paper and heating in a current of hydrogen yields the pure metal.

Properties.—Metallic strontium is yellow, ductile, and somewhat harder than calcium and lead. It has a specific gravity of 2.5. At a low red heat it melts, and if while hot it is exposed to the air it burns brilliantly. When placed in water it decomposes it with some violence. The salts of strontium have great similarity to those of barium. They impart a red color to flame, and were formerly reputed to be poisonous, but this has been found not to be the case.

STRONTIUM AND THE HALOGENS.

Strontium Chloride, $SrCl_2.6H_2O$.—The readiest method of preparing this salt is by saturating hydrochloric acid with the native carbonate and digesting the solution for some time with excess of carbonate, by which metals like aluminum, iron, and manganese are removed. The hot, concentrated solution deposits, on cooling, acicular crystals of the hexagonal system.

These crystals have a sharp, bitterish taste, and deliquesce on exposure to the air. They are soluble in 1.8 parts of water at ordinary temperatures, and in 0.9 part of boiling water; soluble in alcohol.

On the application of heat the salt loses its water of crystallization at 100°, and at 829° it melts. The anhydrous salt is said to be insoluble in absolute alcohol.

Strontium Bromide, $SrBr_2.6H_2O$. **Strontii Bromidum, U. S. P.**—On saturating hydrobromic acid with strontium carbonate the bromide results, as follows:

$$SrCO_3 + 2HBr = SrBr_2 + H_2O + CO_2.$$

If the native carbonate be used as in the preparation of the chloride, then the solution should be digested for some time with a slight excess of the carbonate, in order to remove other bases. The clear solution is concentrated and allowed to crystallize.

Properties.—Strontium bromide occurs in transparent, colorless crystals, odorless, and having a bitter, saline taste, and an alkaline reaction. It is a very deliquescent salt; dissolves in 1.05 parts of water at 15°, and in 0.5 part of boiling water. "It is readily soluble in alcohol, and is precipitated from this solution upon the addition of an equal volume of ether, in which it is insoluble."

On the application of heat the crystals melt in their water of crystallization, and then lose all their water, amounting to 30.4 per cent. The anhydrous salt fuses at 630°.

Strontium Iodide, $SrI_2.6H_2O$. **Strontii Iodidum, U. S. P.**—When hydriodic acid is saturated with strontium carbonate the iodide results, as follows :

$$SrCO_3 + 2HI = SrI_2 + H_2O + CO_2.$$

The solution is filtered, concentrated to a small bulk, and set aside to crystallize. Strontium iodide may also be prepared by saturating a solution of strontium hydrate with iodine in the same manner as in the preparation of potassium iodide. As the result is strontium iodide and iodate, and the latter has to be converted into the former by ignition, it is doubtful if this process is any more economical than the one first given.

Properties.—Strontium iodide is officially described as occuring in "colorless, transparent, hexagonal plates, odorless, and having a bitterish, saline taste. Deliquescent, and colored yellow by exposure to air and light," on which account it is directed to be kept in "dark amber-colored, glass-stoppered vials." The salt is soluble in 0.6 part of water at 15°, and in 0.27 part of boiling water. It is soluble in alcohol, and slightly in ether.

On the application of a gentle heat, the crystals melt in their water of crystallization, and at a higher temperature lose all of their water, amounting to 24.05 per cent. When the temperature approaches redness, the salt is decomposed with loss of iodine, strontium oxide remaining. The aqueous solution is neutral, or very slightly acid, to litmus paper.

STRONTIUM AND OXYGEN.

Strontium Monoxide, SrO.—This compound of strontium may be prepared in small quantity by heating the nitrate, but on a large scale it is obtained by heating the carbonate in large kilns similar to those used in preparing lime.

Properties.—When prepared by heating the nitrate, this compound forms in grayish-white, porous, infusible masses. That made by heating the carbonate is found in the form of powder or pressed into bricks. The latter form is that in which it is best adapted for use in the sugar industry. It is employed to dissolve in water, forming the hydrate, for use in the recovery of certain varieties of sugar.

Strontium Dioxide, SrO_2, is formed when the hydrate is mixed with hydrogen dioxide. It occurs in pearly scales, having the formula $SrO_2.8H_2O$. When these crystals are heated they lose water, leaving the diox-

ide as a light, white powder, in an anhydrous condition, which does not melt at a red heat, but gradually loses oxygen.

Strontium Hydrate, $Sr(OH)_2$, is usually obtained by dissolving the monoxide in water, but it may be prepared in small quantity by precipitation of a solution of strontium nitrate with sodium hydrate. This hydrate is moderately soluble in hot water, and when the hot solution cools, crystals are deposited having the formula $Sr(OH)_2.8H_2O$. The crystals dissolve in 50 parts of cold water and in 2.4 parts of boiling water. On the application of heat the water of crystallization is driven off, and at a higher temperature the hydrate is reconverted into oxide.

OXYGEN SALTS OF STRONTIUM.

Strontium Sulphate, $SrSO_4$, occurs in nature as celestine, in transparent rhombic prisms or in fibrous masses, having the specific gravity 3.89. Celestine usually has a light-bluish shade of color, from which it takes its name. The sulphate may be prepared by adding sodium sulphate to a soluble salt of strontium, as the nitrate. It is soluble in 6895 parts of cold water, and in 9638 parts of boiling water. The salt is quite easily decomposed by boiling it with solution of potassium or sodium carbonate. It fuses when strongly heated.

Strontium Nitrate, $Sr(NO_3)_2$.—This salt is prepared by dissolving strontium carbonate in dilute nitric acid. As ordinarily obtained it separates in anhydrous octohedrons; these are permanent in the air. When a hot, dilute solution of strontium nitrate is allowed to cool slowly, monoclinic prisms or plates separate with 4 molecules of water of crystallization; these crystals readily effloresce on exposure to the air.

The anhydrous salt is easily soluble in water, both hot and cold, but scarcely soluble in alcohol.

On the application of heat the salt melts, and at a red heat is decomposed, a residue of strontium oxide remaining.

The principal use of strontium nitrate is in pyrotechnics. Nearly all red fires contain this salt. The following formula will furnish a good red fire: Strontium nitrate, 50 parts; potassium chlorate, 25 parts; pulverized shellac or sugar, 25 parts; powder separately, and carefully mix without friction. An intimate mixture is best made by passing the powders through a sieve.

Strontium Carbonate, $SrCO_3$, occurs native as strontianite in the form of rhombic prisms. It is prepared by precipitating a soluble salt of strontium with sodium carbonate. The salt is soluble in 18,045 parts of cold water. On gentle ignition it is decomposed, yielding a residue of strontium oxide; this decomposition takes place more readily than in the case of either the barium or calcium carbonate. It may be decomposed by boiling with a solution of ammonium chloride.

The chief use of strontium carbonate is for the purpose of readily furnishing the other strontium salts. It is constantly formed and again converted into oxide in the recovery of sugar from certain varieties of molasses.

Such salts of strontium as have not been described in the preceding

pages may be prepared by processes similar to the corresponding barium or calcium salts.

BARIUM.

Symbol, Ba. *Atomic Weight*, 136.9. *Valence*, II.

History.—The metal barium was first prepared by Davy in 1808, although its compounds were previously well known, and had received the name of baryta.

Occurrence.—Barium sulphate as heavy spar, and barium carbonate as witherite, are the chief natural forms of this metal. More rarely it is found in barytocelestite $(BaSrCa)SO_4$, barytocalcite $(BaCa)CO_3$, and in many ores of manganese, as psilomelane, $(MnBa)O + MnO_2$. A number of silicates contain small quantities of barium, and it is found in some mineral waters. Barium is, further, found in sea water, in sea plants, and in the ash of certain woods, notably that of the beech.

Preparation.—Davy prepared barium by electrolysis of the chloride in the presence of mercury, the resulting amalgam was heated in a tube containing petroleum, whereby the metallic barium was left behind as a white powder. Bunsen succeeded in preparing it by electrolyzing a thick mixture of very dilute hydrochloric acid and barium chloride at a temperature of 100° in the presence of mercury. This resulted in a crystalline barium amalgam, which, on heating, left the barium as a tarnished, porous mass.

Properties.—Barium is a yellowish-white metal, which melts at a red heat. It is not volatile under ordinary circumstances. When exposed to the air it readily oxidizes, and if sufficiently heated takes fire. Its specific weight is about 3.75. When thrown on water, it decomposes it at ordinary temperatures like sodium.

BARIUM AND THE HALOGENS.

Barium Chloride, $BaCl_2.2H_2O$.—The easiest method of preparing this salt is by dissolving native barium carbonate, witherite, in dilute hydrochloric acid. The resulting solution contains, in addition to barium, the chlorides of calcium, iron, manganese, etc. ; these are removed by allowing the solution to remain for some time in contact with an excess of the carbonate, whereby the impurities are precipitated. The clear filtered solution is then neutralized exactly with hydrochloric acid, and evaporated to crystallize.

Commercially, the chloride of barium is prepared by fusing finely-powdered heavy spar with charcoal:

$$BaSO_4 + 4C = BaS + 4CO.$$
$$BaS + 2HCl = BaCl_2 + H_2S.$$

Properties.—Barium chloride occurs in colorless, glistening, rhombic tables, permanent in the air, having a disagreeable, bitterish, saline taste, and a neutral reaction. Like all the other compounds of barium, this salt is heavy, having a specific gravity of 3.05. It is soluble in 2.5 parts of water at 15°, and in about 1.5 parts of boiling water. It is insoluble in concentrated hydrochloric acid and in absolute alcohol. At ordinary temperatures over sulphuric acid the salt loses one molecule of water of crystallization, at 120° it becomes anhydrous, and at a red heat it melts. When it is melted with free access of air it loses chlorine, or, below the melting point, in presence of steam, it gives off some hydrochloric acid, the residue reacting alkaline.

The anhydrous salt on exposure to the air takes up two molecules of water.

Barium chloride is an active poison, although in small doses it has been used some in medicine.

Uses.—The chief uses of barium chloride are as a reagent for the detection and estimation of sulphuric acid, and as a preventive against boiler incrustation.

Barium Bromide, $BaBr_2.2H_2O$, and *Barium Iodide*, $BaI_2.2H_2O$, are known and have been prepared, but appear to have no especial value or use.

BARIUM AND OXYGEN.

Barium Monoxide, BaO, may be obtained by burning the metal in the air; but it is prepared by heating the nitrate in an iron crucible until there is no further evolution of red fumes.

This compound usually occurs as a grayish-white, porous mass, which has a specific gravity of 5.72, and melts at a white heat.

In contact with water it slakes with considerable evolution of heat, forming barium hydrate, $Ba(OH)_2$.

Barium monoxide is used in the manufacture of oxygen by the Brin process.

Barium Dioxide, BaO_2. **Barii Dioxidum**, U. S. P., *Barium Peroxide.*—This compound is prepared by heating the monoxide

in a stream of dry air or oxygen, which is best accomplished at a temperature of about 450°.

Properties.—Barium dioxide occurs as "a heavy, grayish-white, or pale yellowish-white, amorphous, coarse powder, odorless and tasteless. When exposed to the air it slowly attracts moisture and carbon dioxide, and is gradually decomposed. Almost insoluble in cold water, with which, however, it forms a definite hydrate, and to which it imparts a decidedly alkaline reaction."

When heated to bright redness it fuses, and loses one atom of oxygen. Hydrochloric and the other mineral acids decompose it with the formation in the cold of hydrogen dioxide and a barium salt:

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2.$$

Barium dioxide is directed by the Pharmacopœia to be kept in well-closed vessels, and is used for the preparation of the official hydrogen dioxide.

Barium Hydrate, $Ba(OH)_2$.—When barium monoxide is treated with water, the hydrate is formed according to the following reaction:

$$BaO + H_2O = Ba(OH)_2.$$

If just enough water is added to form the compound, the result is a white powder, which at a low red heat melts to an oily liquid, which solidifies on cooling to a crystalline mass. In this condition it has a specific gravity of 4.495, and when dissolved in water forms crystals having the formula $Ba(OH)_2.8H_2O$. These crystals, on exposure to the air, fall to a white powder with a loss of seven molecules of water. On a commercial scale, barium hydrate is prepared by heating the carbonate in a current of steam:

$$BaCO_3 + H_2O = Ba(OH)_2 + CO_2.$$

The resulting mass is dissolved in water, allowed to settle, and the clear solution decanted and crystallized.

It is soluble in 20 parts of water at ordinary temperatures, and in 3 parts of boiling water, forming a strongly alkaline solution, which is extensively used as a reagent under the name of baryta water.

OXYGEN SALTS OF BARIUM AND THE HALOGENS.

Barium Chlorate, $Ba(ClO_3)_2$, is prepared by saturating aqueous chloric acid with barium carbonate. It crystallizes in monoclinic prisms, and is easily soluble in water.

Barium Iodate, $Ba(IO_3)_2$, is obtained by double decomposition between potassium iodate and barium chloride; barium iodate separates out, since

it requires about 3000 parts of water to dissolve it; it is soluble in 600 parts of boiling water. Its chief use is for the preparation of iodic acid.

BARIUM AND SULPHUR.

Barium Monosulphide, BaS, is formed when hydrogen sulphide is passed over heated baryta, as long as water is formed. For the production of larger quantities, an intimate mixture of 100 parts barium sulphate, 25 parts of coal, and 20 parts of common salt is made into a plastic mass with water, dried, and heated for several hours to whiteness.

Properties.—Barium monosulphide is a reddish-white or, from the presence of coal, a grayish-white mass, which in the presence of water is decomposed into barium hydrate and barium sulphydrate, which are dissolved. When a mixture of 5 parts of the barium monosulphide and 1 part of sulphur is boiled with water and allowed to evaporate in a vacuum, colorless crystals separate, having the formula $BaS.6H_2O$.

Barium Sulphydrate, $Ba(SH)_2$, is prepared by passing hydrogen sulphide into a solution of barium hydrate until saturated; by evaporating in a vacuum it crystallizes in white, four-sided prisms.

OXYGEN SALTS OF BARIUM.

Barium Sulphate, $BaSO_4$, *Heavy Spar.*—This is the most abundant native compound of barium, and on that account it furnishes the starting-point in the preparation of the other barium compounds. It is often found in irregular masses, but also comes in well-formed rhombic prisms or tables.

The production of barytes in the United States in 1897 was 27,316 short tons, valued at $24,781.

Barium sulphate is prepared by precipitating any soluble barium salt with dilute sulphuric acid. That made in this manner is extensively used as a pigment in water-colors under the name of *blanc fixe* or *permanent white.*

Properties.—The precipitated salt is a heavy, fine, white powder. It has a specific gravity of 4.53, while that of the native mineral, according to H. Rose, is 4.486. It is almost absolutely insoluble in water, since 1 part requires 400,000 parts of water to dissolve it. In the freshly precipitated state it is soluble in concentrated sulphuric acid, but it is thrown down on dilution with water.

Barium sulphate is decomposed by fusing with three to four times its weight of sodium carbonate, by which barium carbonate and sodium sulphate result; the latter can be removed by solution in water.

In order to precipitate barium sulphate in an impalpable powder, the solution of barium chloride, having a specific gravity of

1.19, is treated in the cold with dilute sulphuric acid having a specific gravity of 1.245; the resulting precipitate is collected, washed with cold water, and sent into commerce in the moist state. This compound is not only used as an unalterable paint, but also for giving weight to cards and paper. The finely-powdered mineral is employed to mix with lead carbonate in the manufacture of the cheaper paints, but, on account of its crystalline character, it has not the covering power of the pure lead compound or of the precipitated barium sulphate.

Barium Disulphate, BaS_2O_7, is prepared by adding finely-powdered barium sulphate to fuming sulphuric acid until it forms a syrupy solution. On heating this to 150° the disulphate deposits in glistening crystals.

Barium Dithionate, $BaS_2O_6.2H_2O$, is prepared by decomposing manganese dithionate with barium sulphide. Its solution on evaporation deposits glittering rhombic crystals. It is soluble in 4 parts of water at ordinary temperatures, and in 1.1 parts of boiling water. Heat converts it into barium sulphate without change of form.

Barium Nitrate, $Ba(NO_3)_2$.—Nitric acid is saturated with barium carbonate or sulphide in order to obtain this salt. As thus prepared it forms permanent, colorless, anhydrous, octohedral crystals. It is soluble in 12 parts of water at ordinary temperatures, and in 3 parts of boiling water; insoluble in alcohol.

Barium nitrate is used as a reagent, but the greatest consumption of it is to furnish the green to colored fires. The following formula will produce a satisfactory color: Potassium chlorate, 50 parts; barium nitrate, 25 parts; sugar or shellac, 25 parts. Each ingredient to be pulverized separately, and then all carefully mixed and run through a sieve. Sulphur is a frequent constituent of colored fires, and may be used in place of the sugar or shellac, but it renders the fires more liable to inflame spontaneously.

Barium Carbonate, $BaCO_3$.—This compound occurs native as witherite, or it may be prepared by adding sodium carbonate to a soluble salt of barium. The native salt occurs in glistening, rhombic crystals, but the precipitated compound is a white powder. It is soluble in 14,000 parts of cold water, and in 15,400 parts at 100°.

When heated to redness barium carbonate loses no carbon dioxide, but in the flame of the oxyhydrogen lamp it melts and gives off this gas slowly. The decomposition takes place more readily and at a lower temperature in the presence of carbon or when steam is passed over it.

CHAPTER III.

THE MAGNESIUM GROUP.

MAGNESIUM.

Symbol, Mg. *Atomic Weight,* 24.3. *Valence,* II.

History.—Attention was first directed to the magnesium salts about the close of the seventeenth century by Grew, a physician of London. He found a peculiar salt in the mineral spring at Epsom, which salt soon became celebrated for its medicinal virtues. The metal was first isolated by Davy, in 1808, although he did not obtain it in a pure condition. Bussy was the first to obtain a distinct quantity of the metal, which he accomplished by acting on the fused chloride with potassium. Bunsen, in 1852, prepared it by electrolysis of the chloride, and Sainte-Claire-Deville and Caron, in 1857, devised a process for its production on a commercial scale. The compounds of magnesium and manganese were not distinguished from each other for a long time, and much confusion regarding them was the result. The distinction was first clearly pointed out by Black, in 1755. Later, magnesium came to be known as the metal existing in *magnesia alba*, and manganese as that in *pyrolusite* (manganese dioxide), then called *magnesia nigra.*

Occurrence.—The metal is not found in the uncombined state in nature. Its compounds, however, are almost as widely distributed as those of calcium, although not in such large quantities. The principal minerals containing it are magnesite, $MgCO_3$; dolomite, $(MgCa)CO_3$; kieserite, $MgSO_4.H_2O$; carnallite, a chloride of magnesium and potassium, $KCl,MgCl_2.6H_2O$; and the following silicates: talc, asbestos, meerschaum, enstatite, and serpentine. Magnesium salts are found in plants, in which they may to a certain extent replace the salts of calcium. As phosphate magnesium is found in the bones and urine of animals.

Preparation.—Magnesium is now usually prepared by the electrolysis of the fused chloride. The decomposition is facilitated by the presence of potassium chloride, so that the mineral carnallite becomes a chief source for it. The precaution must be taken to have no kieserite present, since it is liable to give rise to violent explosions. The electric current employed is furnished

by a powerful dynamo. Magnesium is liberated at the negative pole. The vessel in which the decomposition is effected is made of especially prepared cast-steel, which acts as the negative pole ; the positive pole is made of gas-carbon. In order to prevent the oxidation of the metal, a stream of hydrogen or nitrogen is led through the vessel during the operation.

The metal is also prepared to some extent by throwing into a red-hot crucible 6 parts of anhydrous magnesium chloride, 1 part of fluor-spar, 1 part of sodium and potassium chloride (obtained by fusing together 7 parts of sodium chloride and 9 parts of potassium chloride), and 1 part of finely-cut sodium. A violent reaction ensues, and when this has ended the covered crucible is removed from the fire, and the contents stirred with an iron rod to cause the small particles of magnesium to unite. When cold the metal is removed and washed with water.

The product from both of the preceding processes is quite impure, containing carbon, silicon, and nitrogen. It is purified by distillation from an iron vessel at about 1000°. A stream of hydrogen or coal-gas is passed through the crucible in order to prevent oxidation. The purified metal is pressed into wire by peculiar machinery, and then rolled into ribbon.

Properties.—Magnesium is a silver-white, strongly lustrous metal, having a specific gravity of 1.75. It is unchangeable in dry air, but in the presence of moisture it gradually becomes covered with a film of oxide. When heated without access of air, magnesium melts at about 500° and boils at 1000°. Heated in the air it ignites, and burns with a blinding white light which is especially rich in actinic rays. Water is not decomposed by magnesium at ordinary temperatures, but at 100° decomposition takes place, with evolution of hydrogen and the formation of magnesium oxide.

Uses.—On account of the chemical activity of the magnesium light it is useful in photography, and enters into the composition of the numerous "flash-light" powders. Previous to the development of electric lighting it was used in making strong lights for signalling purposes. It is used in pyrotechny. The celebrated Bengal fires are made as follows : Red—1 part of pulverized shellac, 5 parts of dried strontium nitrate, 2.5 parts of powdered magnesium. Green—1 part of pulverized shellac, 6 parts of dried barium nitrate, 2.5 parts of powdered magnesium.

Magnesium also has some use in the laboratory, where, on account of its freedom from arsenic, it may replace zinc in Marsh's test.

MAGNESIUM AND THE HALOGENS.

Magnesium Chloride, $MgCl_2.6H_2O$. — Sea water and most mineral waters contain magnesium chloride. In the solid state it is found abundantly as carnallite, $KCl,MgCl_2.6H_2O$, at Stassfurt; also in a number of the double salts in that locality. It may be prepared by dissolving magnesite in hydrochloric acid; but, since it is a by-product of not much value in the preparation of potassium chloride from carnallite, it practically all comes from that source.

Properties.—Magnesium chloride occurs in colorless, very deliquescent, monoclinic crystals. It cannot be deprived of its water of crystallization by heat, since, when heated, it decomposes with evolution of hydrochloric acid and formation of magnesium oxychloride.

The anhydrous salt, therefore, is obtained by adding ammonium chloride, evaporating carefully to dryness, and then igniting carefully in a platinum dish to volatilize the ammonium salt; or it may be prepared by drying the crystallized salt in a stream of hydrochloric acid gas.

Anhydrous magnesium chloride occurs in transparent, laminated, pearly plates, which dissolve in water with the evolution of heat. It possesses a bitter, saline taste, and is readily soluble in water. With magnesium oxide it forms an oxychloride which is insoluble in water. If magnesium oxide is added to a 30-percent. magnesium chloride solution to a creamy consistence, the mixture solidifies.

Uses.—Magnesium chloride is used in the preparation of artificial stone, and as a finisher of cotton goods in dye-works.

Magnesium Oxychloride.—When an aqueous solution of magnesium chloride of 1.16 to 1.26 specific gravity is mixed with freshly-prepared magnesium oxide, the mass after some time hardens, so as to be capable of taking a high polish. It has a composition represented by the formula $Mg_{11}Cl_2(OH)_{20}.4H_2O$. On exposure to the air for some time it absorbs carbon dioxide. Another oxychloride is formed when magnesium sulphate, containing ammonium hydrate and chloride, is exposed to the air for some time; the crystalline precipitate, which is deposited, has the composition $Mg_3Cl(OH)_5.4H_2O$.

Anhydrous magnesium chloride forms with alcohol a compound in which the latter replaces the water of crystallization. This crystalline compound, therefore, has the formula $MgCl_2.6C_2H_6O$.

Magnesium Bromide, $MgBr_2.6H_2O$, occurs in sea water and in a number of salt springs. It is this salt more than any other that is the source of

bromine. It may be prepared by heating magnesium in bromine vapor, but a cheaper method consists in passing bromine vapor over an ignited mixture of magnesium oxide and charcoal.

The anhydrous salt forms in solid, white, crystalline masses, which are very deliquescent, and become hot in contact with water. When the salt contains water of crystallization, it loses hydrobromic acid on the application of heat, leaving a residue of magnesium oxybromide.

Magnesium Iodide, MgI_2, occurs associated with the bromide, or it may be prepared by passing iodine vapor over magnesium. It forms very deliquescent, hydrated crystals, which readily decompose with liberation of iodine.

Magnesium Fluoride, MgF_2, is found in nature as the mineral sellaïte. It is insoluble in water. It may be prepared by evaporating magnesium oxide with an excess of aqueous hydrofluoric acid to dryness. It forms amorphous masses, which may be obtained in crystals by fusing with sodium chloride and, after cooling, removing the salt by washing with water.

MAGNESIUM AND OXYGEN.

Magnesium Oxide, MgO. **Magnesia, U. S. P.**—Black, in 1755, appears to have been the first to prepare this oxide. He noted its property of dissolving in sulphuric acid, which served to distinguish it from lime.

Occurrence.—Magnesium oxide is found native in the rare mineral periclase, found at Mount Somma, near Naples. This mineral, however, contains some ferrous oxide.

Preparation.—Magnesia is prepared on a large scale by heating the carbonate. When the light carbonate is ignited, the light or calcined magnesia, *magnesia usta*, results. When a denser carbonate is used, the result is heavy magnesia, **Magnesia Ponderosa, U. S. P.** With the official carbonate the reaction is as follows:

$$(MgCO_3)_4Mg(OH)_2.5H_2O = 5MgO + 6H_2O + 4CO_2.$$

The operation is conducted in iron or earthenware crucibles; at 300° the decomposition readily takes place, and it is known to be complete when a small quantity, taken from the middle of the vessel with an iron spoon and cooled, gives no effervescence with dilute hydrochloric acid.

Probably the most important feature in the successful manufacture of this compound is that of avoiding too high a temperature. In order to prevent parts of the powder from becoming too hot it should be stirred frequently, or it has been recommended to perform the ignition in shallow pans, so that the depth of the carbonate does not exceed 2 to 3 inches. Much also

depends upon the purity and physical condition of the carbonate employed.

Properties.—Official magnesia occurs as a loose, white, odorless powder; possessing an earthy but not a saline taste. It is almost insoluble in water (1 to 55,368), insoluble in alcohol, but readily soluble in dilute acids without effervescence.

The presence of ammonium salts materially increases its solubility in water. In moist air it readily absorbs moisture and carbon dioxide, becoming converted into a basic carbonate.

Magnesia is not visibly affected by any temperature below that of the oxyhydrogen flame, but it will, at lower temperatures, become more dense and crystalline. "On stirring 1 part of Magnesia with 15 parts of water, in a beaker, and allowing the mixture to stand for about half an hour, it will form a gelatinous mass of sufficient consistence to prevent it from dropping out when the glass is inverted."—U. S. P. The heavy magnesia is a denser and finer powder, but in most other characters resembles the light compound.

Magnesium Hydrate, $Mg(OH)_2$, occurs in nature as the mineral brucite. It may be prepared by allowing a not overheated magnesium oxide to stand in contact with water, or more quickly by heating the same compound with water to 150°. Sodium or potassium hydrate precipitates magnesium hydrate from solutions of the salts, like the sulphate or chloride.

Magnesium hydrate is a white, nearly insoluble powder. It is easily soluble in solutions of ammonium salts. At 100° magnesium hydrate is not affected, but when the temperature approaches redness, it is easily converted into oxide. It is sufficiently soluble in water to impart an alkaline reaction to the latter.

SALTS OF MAGNESIUM.

Magnesium Sulphite, $MgSO_3.6H_2O$, is prepared by double decomposition between magnesium sulphate and sodium sulphite; or it may be made by adding sulphurous acid in excess to a mixture of 8 parts of magnesium oxide in 16 parts of water.

Properties.—Magnesium sulphite is a white, crystalline powder, becoming oxidized on exposure to air, odorless, having a slightly bitter, somewhat sulphurous taste, and a neutral or slightly alkaline reaction. It is soluble in 20 parts of water at 15°, and in 19 parts of boiling water; insoluble in alcohol. When heated to 200° the salt loses its water of crystallization, amounting to 50.9 per cent., and is converted into magnesia and anhydrous magnesium sulphate.

Magnesium sulphite was official in the U. S. Pharmacopœia, but was dropped from the last revision. It has some use in medicine, as, on account of its sparing solubility, its taste is not quite so disagreeable as the other sulphites. It has the medicinal properties of the sulphites in general.

Magnesium Sulphate, $MgSO_4.7H_2O$. **Magnesii Sulphas, U. S. P.**—Epsom salt became known about the end of the seventeenth century, because of its valuable purgative qualities, and was designated on the Continent of Europe as bitter salt and *Sal Anglicum.*

Occurrence.—Magnesium sulphate occurs in many mineral waters, the most notable being those of Pullna and Seidlitz, in Bohemia, of Epsom, in England, of Friedrichshall, in Germany, and Hunyadi János, in Hungary. Under the name of kieserite magnesium sulphate is found at Stassfurt, having the composition $MgSO_4.H_2O$. The upper layer of this salt deposit, known as *Abraumsalz*, is a mixture of magnesium sulphate with a number of other salts.

Extraction.—Formerly much magnesium sulphate was obtained by the concentration of natural bitter waters and by the evaporation of the mother liquors after the crystallization of sodium chloride from sea-water. At the present time large quantities are made as a by-product in the manufacture of carbon dioxide for use in mineral waters. Magnesite is used to furnish this gas and sulphuric acid is used to effect its liberation, as follows:

$MgCO_3$	+	H_2SO_4	=	$MgSO_4$	+	CO_2	+	H_2O.
Magnesite.		Sulphuric Acid.		Magnesium Sulphate.		Carbon Dioxide.		Water.

After the escape of carbon dioxide, the residue is dissolved in hot water, neutralized with magnesite, some barium sulphide added, and the mixture allowed to stand for some time in order to separate iron; finally, the clear liquid is concentrated and allowed to crystallize. The *abraumsalz* above mentioned is also employed as a source of magnesium sulphate. This salt is exposed to a damp atmosphere, or suspended in baskets over open evaporators, so that it is brought in contact with the ascending steam; by this means the soluble magnesium and sodium chlorides are dissolved, while the kieserite remains behind. Kieserite is not easily dissolved by water, but on contact with that liquid it disintegrates and is converted into Epsom salt, containing 7 molecules of water; in this form it is dissolved and recrystallized.

Properties.—Magnesium sulphate crystallizes from water in colorless, rhombic prisms, or in small acicular crystals; the latter form is obtained by allowing the crystallization to take place from hot concentrated solutions. The salt is without odor, and has a cooling, saline, bitter taste; the crystals slowly effloresce

in dry air. It is soluble in 1.5 parts of water at 15°, and in 0.7 part of boiling water; insoluble in alcohol. When heated to 52° the salt loses 1 molecule of water, from this temperature up to 132° it loses 5 additional molecules, and at 200° to 238° the remaining molecule is removed and the salt becomes anhydrous. The aqueous solution is neutral to litmus.

With the salts of the alkali metals magnesium sulphate forms double salts, as $MgSO_4.K_2SO_4.6H_2O$; $MgSO_4,(NH_4)_2SO_4.6H_2O$, etc. When anhydrous magnesium sulphate is dissolved in hot concentrated sulphuric acid, six-sided tabular crystals separate out on cooling, which have the composition $MgSO_4.H_2SO_4$.

Uses.—Magnesium sulphate is used in medicine as an active and safe cathartic. It also has some use in dyeing and calico printing as a finisher. When this salt is used with aniline colors, the finished goods are found to better resist the action of soap.

Magnesium Nitrate, $Mg(NO_3)_2.6H_2O$, is prepared by neutralizing nitric acid with magnesium carbonate. It forms deliquescent monoclinic prisms or acicular crystals. From hot solutions it separates with 2 molecules of water of crystallization. The crystals are soluble in 0.5 part of water at 15°, and in 9 parts of alcohol.

Normal Magnesium Phosphate, $Mg_3(PO_4)_2$, is found in bones, in the seeds of many plants, and in a number of minerals. It is precipitated when a solution of trisodium orthophosphate is added to one of magnesium sulphate. One part of the salt requires 5000 parts of water to dissolve it.

Magnesium Hydrogen Phosphate, $MgHPO_4$, is formed when a solution of ordinary sodium phosphate, Na_2HPO_4, is added to one of magnesium sulphate. On standing in contact with water, this precipitate becomes crystalline with 7 molecules of water. One part of this crystalline precipitate is soluble in 322 parts of water.

Ammonium Magnesium Phosphate, $Mg(NH_4)PO_4.6H_2O$.—This salt frequently separates from decomposing urine, and large crystals of it have been found in some varieties of guano. It is formed when ammonium chloride and hydrate are mixed with a solution of magnesium sulphate, and then a solution of a soluble phosphate added. The crystals which are thus produced are transparent, quadratic prisms, soluble in 15,000 parts of water at 15° and in 44,000 parts of ammoniacal water. At 100° five molecules of water are given off without loss of ammonia, and at higher temperatures the remainder of the water and the ammonia escape, leaving magnesium pyrophosphate, $Mg_2P_2O_7$.

Magnesium Arsenate and *Magnesium Ammonium Arsenate* are similar in their method of preparation and properties to the corresponding phosphates.

Magnesium Borate.—When solutions of borax and magnesium sulphate are mixed in the cold, no precipitation takes place, but on long

boiling a precipitate forms having the composition $Mg(BO_2)_2,2Mg(OH)_2.7H_2O$. This compound has had some use as an antiseptic.

Magnesium Carbonate, $MgCO_3$.—This is the normal magnesium carbonate, and is found abundantly in nature as magnesite. It is somtimes found in rhombohedral crystals, which are isomorphous with those of calcite. In pharmacy and medicine we are concerned chiefly with the artificially prepared or basic magnesium carbonate $(MgCO_3)_4,Mg(OH)_2.5H_2O$, **Magnesii Carbonas**, U. S. P. This compound became known as a valuable medicinal agent about the beginning of the eighteenth century, under the name of *magnesia alba*

Preparation.—10 parts of magnesium sulphate and 12 parts of sodium carbonate are each dissolved separately in 80 parts of distilled water, the solutions are mixed in the cold, and the mixture boiled for 15 minutes. The precipitate is collected on a muslin filter and washed with hot water until the washings cease to give a reaction with barium chloride for sulphuric acid. The heavy carbonate of magnesia, *magnesia carbonas ponderosa* of the British Pharmacopœia, is prepared by dissolving each of the above salts in 20 parts of water, mixing, and evaporating the resulting mixture to dryness. The dry residue is then washed thoroughly with hot water until all sodium sulphate is removed. The product is a dense powder. The reaction which takes place in these processes is as follows :

$$\underset{\text{Magnesium Sulphate.}}{5MgSO_4} + \underset{\text{Sodium Carbonate.}}{5Na_2CO_3} + \underset{\text{Water.}}{6H_2O} = \underset{\text{Official Magnesium Carbonate.}}{(MgCO_3)_4,Mg(OH)_2.5H_2O} + \underset{\text{Sodium Sulphate.}}{5Na_2SO_4} + \underset{\text{Carbon Dioxide.}}{CO_2}.$$

The method of Pattinson consists in igniting dolomite, a magnesium and calcium carbonate, and treating the product with solution of carbon dioxide under a pressure of 5 to 6 atmospheres. The magnesium carbonate goes into solution much easier than the calcium carbonate. The clear solution is separated from the precipitate of the latter, and on heating deposits a precipitate of the official carbonate, with evolution of some carbon dioxide, which may be used again.

Properties.—The official magnesium carbonate comes in commerce in loose, white, easily-pulverized masses, which are readily reduced to a fine, white, amorphous powder, without odor, having an earthy taste, and permanent in the air. It dissolves in 2500 parts of cold water, and in 9000 parts of hot water, and

imparts to the water an alkaline reaction ; alcohol exerts no solvent action upon it. Dilute acids dissolve it with active effervescence, and without leaving any residue.

Solution of ammonium salts have considerable solvent action on magnesium carbonate, and in the presence of ammonium chloride no precipitation of the carbonate will occur.

On the application of heat, water is first given off, and at 170° (Mendelejeff) the decomposition of the carbonate is complete, magnesium oxide remaining. This is considerably lower than the temperature of dissociation given by other authorities, and would consequently require more time than that usually given for the preparation of magnesium oxide.

When the official magnesium carbonate is shaken with water until a uniform mixture results, and carbon dioxide is passed in, there results a clear solution of *acid magnesium carbonate*, $MgH_2(CO_3)_2$, which has not been separated in the solid state. This solution on exposure to the air, and warming to 50°, deposits crystals of the neutral carbonate with 3 molecules of water, $MgCO_3.3H_2O$, or at a winter temperature $MgCO_3.5H_2O$ separates. Under ordinary atmospheric pressure 1 part of magnesium carbonate requires 761 parts of carbonic acid water to dissolve it, under 3 atmospheres of pressure the solubility is 1 to 134, and at 6 atmospheres it is 1 to 76 of the carbonic acid water.

The *Liquor Magnesii Carbonatis* of the British Pharmacopœia is such a solution, and contains about 2 per cent. of the official carbonate. It is clear, and free from bitter taste.

Uses.—Magnesium carbonate is used in medicine as an antacid, and in the presence of acids becomes cathartic in its action.

Magnesium Silicates.—A number of these compounds occur widely distributed in the mineral kingdom. Talc has the composition $3MgSiO_3.H_2SiO_3$, serpentine $3MgO,2SiO_2.2H_2O$, etc.

BERYLLIUM (Glucinum, Gl).

Symbol, Be. *Atomic Weight*, 9.03. *Valence*, II.

Historical.—The mineral beryl was formerly supposed to be a compound of silica with calcium or aluminum, but Vauquelin, in 1798, showed the base to be different from both of these, and the name glucina was given to this new earth. Wöhler, in 1828, first obtained the metal, by fusing the chloride with potassium.

Occurrence.—Beryllium occurs in nature in a few rare minerals. Beryl is a silicate of beryllium and aluminum, $3BeSiO_3,Al_2(SiO_3)_3$, which

occurs in beautiful hexagonal crystals of a green color; the transparent, green-colored varieties are known as emerald, and those of a bluish-green tint are termed aquamarine. Phenacite is a beryllium silicate of the composition Be_2SiO_4, and chrysoberyl is a beryllium and aluminum oxide, BeO,Al_2O_3.

Preparation.—Metallic beryllium is prepared by passing the vapor of beryllium chloride, along with hydrogen, over heated sodium. A violent reaction occurs, and the chloride is reduced to the metallic state and is obtained in the form of powder. It is afterwards caused to cohere by fusing in a crucible under a layer of sodium chloride. Any of the modern processes for the preparation of aluminum may be successfully applied to the preparation of beryllium.

Properties.—Beryllium is a silver-white, lustrous metal; malleable, and having the specific gravity 1.64. It remains unchanged in the air at ordinary temperatures, but when heated it becomes coated with a thin film of oxide which prevents further change. If the metal be in a finely-powdered state it will inflame when heated in the air. It does not act upon water, even when the latter is boiled with it. Dilute acids, like hydrochloric and sulphuric, dissolve it, as do also the hydrates of sodium and potassium, but nitric acid, even when hot and concentrated, acts on it very slowly.

Beryllium Chloride, $BeCl_2$, is obtained in the anhydrous condition by passing chlorine over a heated mixture of beryllium oxide and charcoal. It is easily fusible and volatile, and may be obtained with 4 molecules of water of crystallization from aqueous solution. The chloride may also be obtained by dissolving the oxide in hydrochloric acid. In many of its characters it resembles magnesium chloride.

Beryllium Bromide, $BeBr_2$, *Iodide*, BeI_2, and *Fluoride*, BeF_2, are known, and may be prepared like the chloride.

Beryllium Oxide, BeO, yields with acids salts having a sweet taste. The solutions of these salts give precipitates of the *hydrate*, $Be(OH)_2$, on the addition of sodium or potassium hydrate; this hydrate is distinguished from that of magnesium by being soluble in excess of the reagent, and from the hydrate of aluminum by its solubility in excess of alkali carbonate.

Beryllium Sulphate, $BeSO_4.4H_2O$, separates from hot, concentrated solutions, while from acid solution $BeSO_4.7H_2O$ crystallizes; it is isomorphous with magnesium sulphate.

Beryllium Nitrate, $Be(NO_3)_2.3H_2O$, is an extremely deliquescent salt, easily soluble in alcohol.

Beryllium Phosphate, $BeHPO_4.3H_2O$, is obtained by precipitating a soluble salt of beryllium with sodium phosphate.

Beryllium Carbonate, $BeCO_3.4H_2O$, separates in crystals of this composition, when a solution of the basic carbonate in carbon dioxide is concentrated over sulphuric acid with exclusion of oxygen.

ZINC.

Symbol, Zn. *Atomic Weight*, 65.10. *Valence*, II.

History.—Paracelsus in the sixteenth century first recognized zinc as a metal. It was known, however, long before that time that certain ores of zinc known as *cadmia* would, when smelted with copper ores, furnish a yellow metal (brass). Works for the preparation of metallic zinc were first established in the year 1743, at Bristol, England.

Occurrence.—It is doubtful if zinc occurs in nature in the metallic state, although it is said to have been found in Australia. The most abundant ore of zinc is the sulphide, or zinc blende, and next the silicate, or calamine, although the carbonate (smithsonite) is often included under the same general term. The most noted European localities are Belgium, Silesia, Saxony, and England. In the United States fully half the zinc is produced in Missouri, although there are important deposits in Pennsylvania, New Jersey, Virginia, Wisconsin, Kansas, and Arkansas.

In the United States there are two ores that are peculiar to the localities named and are not found abroad,—namely, the native oxide, called red oxide, or zincite, and a mixture of zinc oxide with manganese and iron oxide, known as franklinite. Both of these minerals occur at Franklin and Mine Hill, New Jersey.

Zinc has been found in the ashes of some plants which grow in localities where the soil contains the metal.

Preparation.—Zinc ores are first roasted to remove carbon dioxide and water in the case of calamine, and in the blende to convert the sulphide into oxide. The roasted ore is then reduced with charcoal.

Originally the English process was exclusively employed. This consisted in mixing the roasted ore with half its weight of charcoal, and heating in crucibles which were constructed with a tube extending from the bottom of the crucible down to a vessel underneath. This tube was plugged at its opening into the crucible with a piece of wood which was converted early in the operation into porous charcoal, and thus allowed the passage of the zinc vapor down to the receiver below. The top of the crucible was tightly covered. The English process has now given way to the Belgian and the Silesian processes.

The Belgian process is illustrated in the figures as follows: Fig. 122 shows a side view of the retorts placed in the furnace,

and Fig. 123 gives a back view of these retorts, showing how the fire reaches them.

FIG. 122.

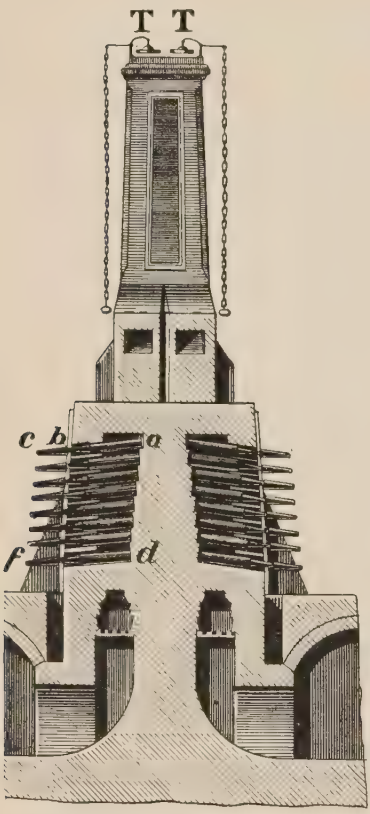
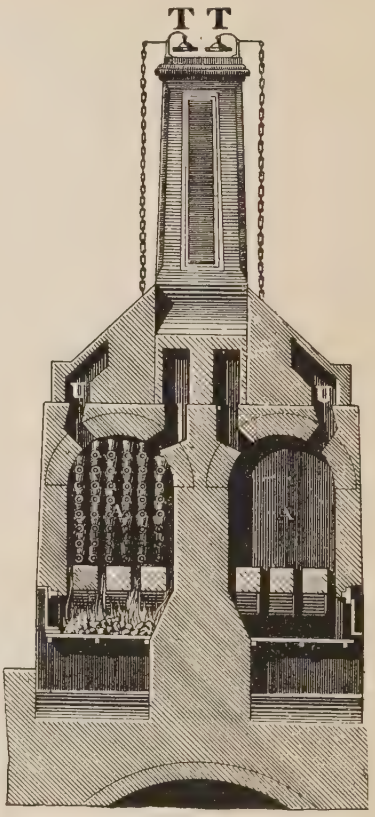


FIG. 123.

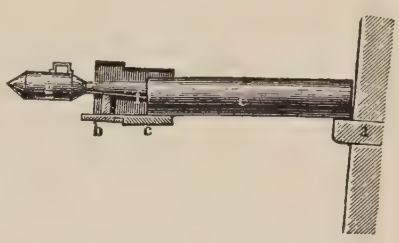


Zinc smelting (Belgian process).

The retorts *e*, Fig. 124, are made of fire-clay, and filled with a mixture of powdered coal and roasted ore. They are about 1 meter in length, with an internal diameter of 0.2 meter. To the open end a conical earthenware tube 0.24 meter in length is luted, and to it the condenser, *g*, is fitted; this condenser has a small opening in its end to permit the escape of gases. The charge consists of about 40 pounds of a mixture of 2 parts of roasted ore and 1 part of coal. About 48 of the crucibles are placed in one of the furnaces. On the application of heat car-

bon monoxide first escapes, and burns at the mouth of the tube (*f*, Fig. 124) with a blue flame. As the metal begins to volatilize the flame becomes much whiter in color; the receiver *g* is then placed in position, and there is condensed in it a mixture of finely-divided metal and oxide ; this is removed after a time, and the metal collected both in the receiver and in the earthenware tube.

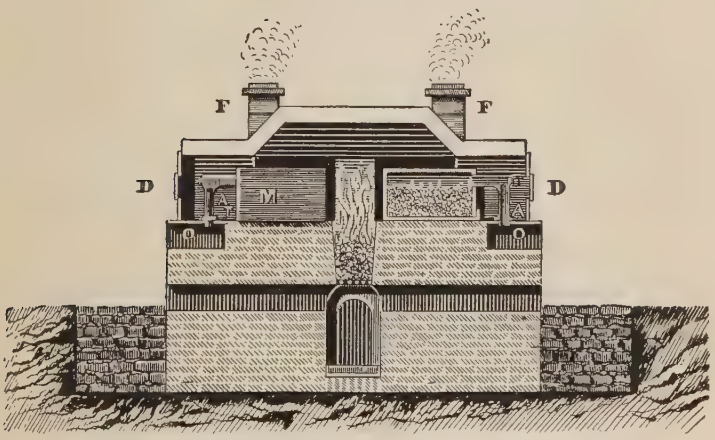
FIG. 124.



Retort of Belgian process.

In the Silesian process is used a retort or muffle of a shape different from that employed in the Belgian method, and it is considerably larger in size. Figs. 125 and 126 show these muffles in

FIG. 125.



Zinc smelting (Silesian process).

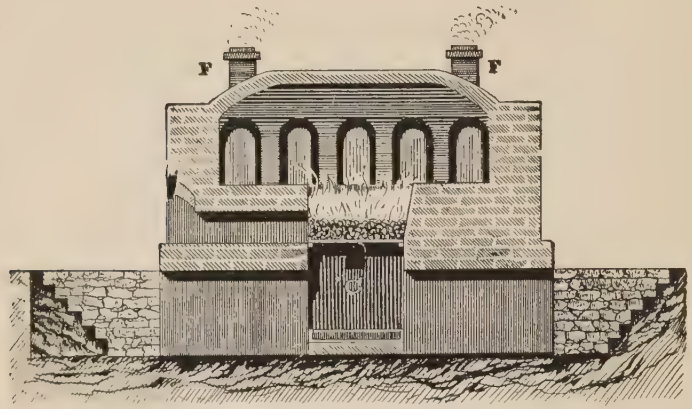
position in the furnace, while an enlarged view of a muffle is shown in Fig. 127.

In this process considerably more of the zinc is converted into oxide. A few furnaces are constructed to use the Silesian muffles below and the Belgian retorts above. Gas is sometimes used for fuel.

Commercial zinc often contains as impurities lead, carbon, iron, arsenic, and some other metals. It, therefore, requires further

purification. This is accomplished by submitting it to distillation in retorts similar to those used in the English method of reduction; that is, with an exit-pipe cemented into the bottom

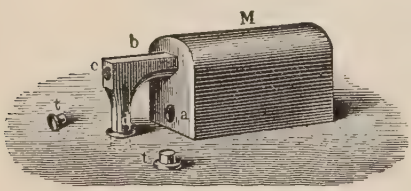
FIG. 126.



Zinc smelting (Silesian process).

of the vessel. The vapors pass down through this tube and are collected in a vessel beneath. Zinc purified in this manner is usually remelted and cast into rods, rolled into thin sheets, or granulated by pouring into cold water, in which form it is known as "mossy" zinc.

FIG. 127.



Crucible of Silesian process.

The Belgian process is chiefly used in the United States, where the output for 1897 amounted to 100,103 short tons, valued at $8,095,717. Of this production 12,455 tons was exported.

Properties.—Zinc is a bluish-white metal, with a lustre which is almost insignificant when compared with that of some other metals. When cast it exhibits a tabular structure. Its specific gravity ranges from 6.9, when it is cast, to 7.2, when it is rolled. It is very ductile, considering its hardness. Its malleability is considerable when pure, but in the impure condition it is quite brittle.

When heated to 100° and not above 150°, its malleability and ductility are materially increased; above 200° it becomes suffi-

ciently brittle to be powdered in an iron mortar. Zinc melts at 412° to 415°, and at 940° it boils. It is official under the name of **Zincum,** and this metal should dissolve in dilute hydrochloric or sulphuric acid with evolution of hydrogen, and without leaving an appreciable residue. The purest metal is slowly attacked by sulphuric acid, but the action may be hastened by the addition of a little platinic chloride, to establish galvanic action; the hydrogen evolved should have no disagreeable odor.

Zinc does not readily undergo change when exposed to dry air; in damp air it becomes coated with a thin film of oxide and carbonate, which prevents further action.

Water is not decomposed by zinc at ordinary temperatures, but at 100° slight action takes place, which becomes correspondingly greater as the temperature is increased.

Sodium and potassium hydrates dissolve zinc with evolution of hydrogen and formation of sodium and potassium zincate. Zinc-dust is composed chiefly of a finely-powdered zinc mixed with some oxide. It is a valuable reducing agent in the laboratory, and is used on a commercial scale in the reduction of indigo. It has also some use as a paint.

Uses.—Zinc is used in large quantities in the manufacture of brass. It is also employed in desilvering lead, in galvanizing, in batteries, for roofing, and a great number of other purposes.

ZINC AND THE HALOGENS.

Zinc Chloride, $ZnCl_2$. **Zinci Chloridum,** U.S.P., may be obtained by burning strips of the metal in chlorine gas, and by evaporating the solution of zinc chloride and distilling the residue.

Liquor Zinci Chloridi, U. S. P., is prepared by dissolving the metal in hydrochloric acid to saturation; a small quantity of nitric acid is then added to oxidize any impurity of iron, and the solution is evaporated to a dry mass at a temperature not exceeding 115°. The residue is dissolved in water and allowed to stand in contact with the zinc carbonate for 24 hours; the clear, supernatant liquid is then siphoned off and brought to a strength of 50 per cent.

Since zinc oxide is to be had in commerce of great purity and at a reasonable price, it is probably almost as economical to prepare the chloride by saturating the acid with oxide as follows:

$$\underset{\text{Zinc Oxide.}}{ZnO} + \underset{\text{Hydrochloric Acid.}}{2HCl} = \underset{\text{Zinc Chloride.}}{ZnCl_2} + \underset{\text{Water.}}{H_2O.}$$

The dilute solution of zinc chloride may be filtered through paper, but when more concentrated it should be filtered through asbestos, or allowed to stand until clear and then decanted.

In order to obtain the dry salt, the solution is evaporated in a porcelain dish on a sand-bath until it becomes syrupy, and is then carefully brought to dryness. Some oxychloride is formed during the evaporation, which may be diminished by the cautious addition of hydrochloric acid from time to time. The dried salt may be still further purified by distillation.

Properties.—Zinc chloride is found in commerce as a white, granular powder, or in irregular, porcelain-like masses, or it may be obtained moulded into sticks. It is odorless, intensely caustic, and, when dissolved in sufficient water to make tasting possible, has an astringent, metallic taste. It is very deliquescent; soluble in 0.3 part of water at 15°, and very soluble in alcohol. When heated to 115° the salt melts, and at a higher temperature it is volatilized with some decomposition, leaving a residue of oxychloride and oxide. The official salt leaves a clear solution with water, and this solution on prolonged boiling deposits a basic salt. The syrupy solution, on the addition of a few drops of hydrochloric acid, deposits octohedral crystals, containing one molecule of water of crystallization. The official solution has a specific gravity of 1.535 at 15°, and reacts acid with litmus paper.

The concentrated, aqueous solution attacks cellulose, and cannot, therefore, be filtered through paper.

Uses.—Zinc chloride in solution is largely used as an antiseptic and disinfectant. It enters into the composition of most embalming fluids, and constitutes the well-known Burnett's disinfecting liquid. A solution of 100 parts of zinc chloride in 12 parts of water, saturated with 6 parts of potassium iodide, and then as much iodine added as the solution will dissolve, furnishes a valuable microscopic reagent for cellulose, with which it gives a blue color. A commercial solution of calamine, zinc blende, or the impure metal in hydrochloric acid, is used to impregnate wood to effect its preservation. The purified salt has some use in medicine as an antispasmodic and alterative, and also as an escharotic.

Zinc Bromide, $ZnBr_2$. **Zinci Bromidum,** U.S.P.—The aqueous solution is easily prepared by gently warming a mixture of zinc, bromine, and water. The same precautions are to be observed, in obtaining the dry salt from this solution, that were

noted under the chloride. The dry salt may be purified by sublimation, when it is obtained in white, acicular crystals.

Properties.—Zinc bromide is found as a white, granular powder, odorless, and having a sharp, saline, and metallic taste. It is a very deliquescent salt, readily soluble in water and alcohol. On the application of heat the salt fuses at 394°, and at higher temperatures it sublimes. The aqueous solution reacts acid toward litmus paper.

The chief use of zinc bromide appears to be for the treatment of epilepsy.

Zinc Iodide, ZnI_2. **Zinci Iodidum**, U. S. P.—Zinc and iodine readily unite when heated together, and the salt may, by this process, be obtained in the solid state, which, on heating, yields the salt as a sublimate of white, acicular crystals. A watery solution is obtained by digesting a mixture of 1 part granulated zinc, 3 parts of iodine, and 10 parts of water. When the watery solution is evaporated in a vacuum it yields the salt in octohedral crystals.

Properties.—Zinc iodide occurs as a white, granular powder, odorless, and having a sharp, saline, and metallic taste. It is very deliquescent, and, when exposed to the air, first liquefies, and then absorbs oxygen, with liberation of iodine and the production of a brown color. Water, alcohol, and ether all readily dissolve it. The aqueous solution reddens blue litmus paper. On the application of heat to zinc iodide it melts at about 440°, and at a higher temperature it sublimes with some decomposition, forming quadratic needles, and leaving a residue of zinc oxide.

Zinc iodide has some use in medicine.

ZINC AND OXYGEN.

Zinc Oxide, ZnO. **Zinci Oxidum**, U. S. P.—Zincite, or red oxide of zinc, occurs with other zinc minerals at Mine Hill, New Jersey. Its red color appears to be due to manganese.

Zinc oxide is prepared on a large scale by heating the metal in earthenware retorts; the vapors in contact with air ignite, and are conducted into large chambers, where deposition of the oxide takes place. The product is the commercial zinc white. For pharmaceutical purposes the oxide is usually prepared by heating the basic carbonate to low redness, when the following reaction takes place:

$$\underset{\text{Basic Zinc Carbonate.}}{2ZnCO_3.3Zn(OH)_2} = \underset{\substack{\text{Zinc}\\\text{Oxide.}}}{5ZnO} + \underset{\substack{\text{Carbon}\\\text{Dioxide.}}}{2CO_2} + \underset{\text{Water.}}{3H_2O}$$

It is stated that a temperature of 280° to 300° is sufficient to accomplish the above reaction; too high a temperature does not yield as satisfactory a product. The oxide was formerly known as *Lana Philosophica*, *Nihilum Album*, and *Nix Alba*.

Properties.—Zinc oxide is a white, amorphous powder, without odor or taste. It is insoluble in water or alcohol, but is soluble, without effervescence, in dilute acids; it is also soluble in ammonia water, and in solution of ammonium carbonate. When heated zinc oxide becomes yellow in color. It is practically infusible, but in a stream of oxygen, at very high temperatures, it becomes crystalline in character. On exposure to the air it gradually absorbs carbon dioxide.

Uses.—Zinc oxide, when ground with oil, is extensively used as a paint. It has the advantage of not darkening in the presence of sulphur compounds. It is also less injurious to the workmen. It is one of the most economical and satisfactory compounds from which to prepare the various salts of zinc, and is considerably used in medicine.

The production of zinc oxide in the United States in 1897 was 26,275 short tons, valued at $2,102,000.

Zinc Hydrate, $Zn(OH)_2$, is obtained as a white precipitate when sodium or potassium hydrate is added to a solution of zinc sulphate. It is readily soluble in excess of the reagent, forming zincates, as $Zn(ONa)_2$.

When the above zincate solution is boiled the hydrate is thrown down.

On immersing a strip of zinc in ammonia water the hydrate is slowly deposited in the form of rhombic prisms.

OXYGEN SALTS OF ZINC.

Zinc Sulphate, $ZnSO_4.7H_2O$. **Zinci Sulphas**, U. S. P.—Under the name of white vitriol this salt was known in the fifteenth century. It was prepared by lixiviation of roasted zinc blende, a process which is used on the large scale at the present time.

The sulphate is also made by dissolving the metal or zinc white in dilute sulphuric acid, and purifying by recrystallization:

$$\underset{\text{Zinc Oxide.}}{ZnO} + \underset{\text{Sulphuric Acid.}}{H_2SO_4} = \underset{\text{Zinc Sulphate.}}{ZnSO_4} + \underset{\text{Water.}}{H_2O.}$$

Of course an indefinite amount of water is used in this reaction.

Properties.—Zinc sulphate, containing 7 molecules of water of crystallization, occurs in colorless, transparent, rhombic crystals, without odor, and with an astringent, metallic taste. The

crystals effloresce in dry air. The salt is soluble in 0.6 part of water at 15°, and in 0.2 part of boiling water, also soluble in 3 parts of glycerin, but insoluble in alcohol.

It melts in its water of crystallization when rapidly heated, and may be partly decomposed at higher temperatures. On applying heat gradually, 5 molecules of water are driven off at 50° (31.3 per cent.) without melting. At 100° the sixth is lost, and at 110°, in a current of dry air, the salt becomes anhydrous. It loses 6 molecules of water in a vacuum. Monoclinic crystals, containing only 6 molecules of water, may be obtained by having crystallization take place from concentrated solutions and above 30°. A salt having the composition $ZnSO_4.H_2O$ may also be obtained from the hot, concentrated solution. The aqueous solution of zinc sulphate has an acid reaction. Basic salts may be obtained by boiling concentrated solutions of zinc sulphate with metallic zinc or with zinc oxide.

Uses.—Zinc sulphate is used in medicine ; in small doses as a tonic and astringent, in larger doses as an emetic. It has the property, common to all the other zinc salts, of acting as an irritant poison in large doses. The salt is also used in finishing cotton goods.

Zinc Nitrate, $Zn(NO_3)_2.6H_2O$, forms deliquescent crystals when 1 part of zinc oxide is dissolved in 6.5 parts of nitric acid of 25-per-cent. strength. The process by which the metal is dissolved in nitric acid is not employed, since a part of the acid is decomposed and lost in the reaction. The crystals of zinc nitrate form in colorless, striated, four-sided prisms, very soluble in water and in alcohol. When heated, the salt loses nitric acid and becomes converted into a basic nitrate.

Zinc Hypophosphite, $Zn(H_2PO_2)_2.H_2O$, is formed by dissolving zinc oxide in hypophosphorous acid and evaporating. It forms in permanent, rhombohedric crystals.

Zinc Phosphate, $Zn_3(PO_4)_2.4H_2O$, is obtained as a white, nearly insoluble precipitate, by the addition of sodium phosphate solution to a solution of zinc sulphate :

$$2Na_2HPO_4 + 3ZnSO_4 = Zn_3(PO_4)_2 + 2Na_2SO_4 + H_2SO_4.$$

This precipitate is gelatinous when first formed, but becomes crystalline on standing.

Zinc Arsenite, $Zn(AsO_2)_2$, and *Zinc Arsenate*, $Zn_3(AsO_4)_2.3H_2O$, are known. The latter in many respects resembles the phosphate.

Zinc Silicate, Zn_2SiO_4, occurs native as willemite, and the same compound, with 1 molecule of water, occurs as silicious calamine.

Zinc Carbonate. **Zinci Carbonas Præcipitatus**, U. S. P.—This compound is officially defined as "an impalpable powder,

of somewhat variable chemical composition." The true carbonate, $ZnCO_3$, occurs native as zinc-spar, in hexagonal prisms, and massive as smithsonite, hardly to be distinguished from calamine. It may be prepared by precipitating a solution of zinc sulphate in the cold with a solution of acid potassium carbonate in excess.

The official basic carbonate is not of constant composition, but is generally expressed as consisting of 2 molecules of normal zinc carbonate and 3 molecules of zinc hydrate, $2ZnCO_3.3Zn(OH)_2$.

To prepare it, 1 part of sodium carbonate is dissolved in 10 parts of water and heated to the boiling point; to it is then added, in a thin stream so as not to interfere with the boiling, a solution of 1 part of zinc sulphate in 10 parts of water. The proportions should be such that, after all the zinc solution has been added, the mixture has a weak, alkaline reaction. The following expresses the reaction which occurs:

$$\underset{\text{Zinc Sulphate.}}{5(ZnSO_4.7H_2O)} + \underset{\text{Sodium Carbonate.}}{5(Na_2CO_3.10H_2O)} = \underset{\text{Basic Zinc Carbonate.}}{2ZnCO_3.3Zn(OH)_2} + \underset{\text{Sodium Sulphate.}}{5Na_2SO_4} + \underset{\text{Carbon Dioxide.}}{3CO_2} + \underset{\text{Water.}}{82H_2O.}$$

The precipitate is first washed with hot water by decantation, and afterwards collected on a filter and washed with hot water until the washings cease to give a reaction with barium chloride.

Properties.—Basic zinc carbonate is an impalpable, amorphous powder, permanent in the air, and almost absolutely insoluble in water or alcohol; dilute acids, ammonia water, and solution of ammonium carbonate dissolve it freely. It is also soluble in water containing carbon dioxide. At about 300° the salt loses water and carbon dioxide, and is converted into zinc oxide, which is yellow while hot, but becomes white when cold.

Zinc Sulphide, ZnS.—Zinc blende is found native in crystals, belonging to the regular system, or massive. The color varies from a light brown to a deep black, depending on the amount of iron present. It is also rarely found in nature as the mineral wurtzite, in hexagonal prisms.

When hydrogen sulphide is passed into a neutral solution of a zinc salt, the sulphide is formed as a white, amorphous precipitate. This may be converted into hexagonal crystals by heating in a current of hydrogen, or when zinc oxide is heated in a current of hydrogen sulphide.

Zinc sulphide is soluble in the dilute mineral acids, but insoluble in acetic acid.

Zinc Phosphide, Zn_3P_2, **Zinci Phosphidum**, U. S. P., is obtained as a gray mass by heating powdered zinc in the vapor of

phosphorus. It should be preserved in small, glass-stoppered vials. Zinc phosphide is "a gritty powder of a dark gray color, or crystalline fragments of a dark, metallic lustre, and having a faint odor and taste of phosphorus. In contact with the air it slowly emits phosphorous vapor.

"Insoluble in water or alcohol. Soluble in diluted hydrochloric or sulphuric acid with evolution of hydrogen phosphide.

"When strongly heated, with exclusion of air, it melts, and finally sublimes. When heated in air, it becomes oxidized to zinc phosphate."—U. S. P.

Uses.—Zinc phosphide is employed in medicine. Its physiological properties so closely resemble those of phosphorus that it is used as a convenient method of administering that element.

CADMIUM.

Symbol, Cd. *Atomic Weight*, 111.5. *Valence*, II.

History.—Cadmium was discovered in 1817 by Stromeyer of Göttingen. Hermann of Schönebeck discovered it independently and at about the same time.

Occurrence.—Cadmium is found in small quantity in a number of zinc ores, and chiefly as sulphide. The fibrous zinc blende found at Przibram, Bohemia, contains from 2 to 3 per cent. of cadmium. The rare mineral greenockite consists almost entirely of cadmium sulphide. It is found at Bishopstown, in Scotland, at the Ueberoth zinc mine near Friedensville, in Pennsylvania, and at Granby and Joplin, Missouri.

Preparation.—In the preparation of zinc from ores which contain cadmium the latter metal distils first, and by saving this first portion, mixing it with coal, and distilling it at the lowest possible temperature, a distillate is obtained very rich in cadmium, while the zinc remains behind. This is rendered possible by the boiling point of cadmium being 760°, while that of zinc is 940°. The cadmium is finally separated from the zinc by dissolving in hydrochloric acid, having the latter in slight excess, and passing in hydrogen sulphide; the cadmium sulphide is precipitated, while the zinc remains in solution in the presence of the free acid. The cadmium sulphide is dissolved in hot concentrated hydrochloric acid, and the cadmium precipitated as carbonate by an excess of solution of ammonium carbonate, by which means the copper and arsenic are retained in solution. The cadmium carbonate is washed, dried, and converted by heat into cadmium oxide, which, by distillation with coal, yields the metal.

Properties.—Cadmium is usually found in commerce in sticks. It is a white, lustrous metal, with a fibrous fracture. When pure it is malleable and ductile. Its specific gravity is 8.6 to 8.7. It melts at 320.7°, and boils at 760°. When heated with access of air it burns, giving off a brown vapor. Most of the acids dissolve it readily. Its salts are colorless. In many of their properties the salts of cadmium are identical with those of zinc.

COMPOUNDS OF CADMIUM.

Cadmium Chloride, $CdCl_2.2H_2O$, *Cadmium Bromide*, $CdBr_2.4H_2O$, and *Cadmium Iodide*, CdI_2, are colorless, soluble salts, which are prepared similarly to the corresponding zinc salts. The chloride is made by dissolving the metal or oxide in hydrochloric acid, while the bromide and iodide are prepared by digesting the metal with bromine and iodine respectively in the presence of water. These salts are moderately soluble in alcohol, easily soluble in water, but not deliquescent. They form double salts with the salts of the alkalies, and cadmium potassium iodide, $CdI_2,2KI.2H_2O$, is a useful reagent for alkaloids. Cadmium iodide has some use in photography.

Cadmium Oxide, CdO, forms as a brown, infusible, amorphous powder, when cadmium is burned in the air, or by ignition of the carbonate or nitrate.

Cadmium Hydrate, $Cd(OH)_2$, is prepared by precipitation of a soluble cadmium salt, by potassium or sodium hydrate. It forms, when collected and dried, a white, amorphous powder, which at 300° loses water and is converted into oxide.

Cadmium Sulphate, $CdSO_4$.—This salt was official in the Pharmacopœia of 1870, but since that time it and the other salts of cadmium have practically ceased to have any use in medicine. To prepare this salt, 10 parts of cadmium in small pieces are placed in a porcelain dish with 10 parts of pure sulphuric acid and 40 parts of water. The mixture is warmed until solution is effected, and the sôlution is filtered and evaporated to crystallize. On account of the slowness with which sulphuric acid acts on cadmium, the metal is sometimes first dissolved in nitric acid, and the hydrate is precipitated from the resulting nitrate by sodium hydrate, and then dissolved in the sulphuric acid.

Properties.—Cadmium sulphate crystallizes in large, colorless, monoclinic crystals, having the composition $3CdSO_4.8H_2O$. They are permanent in the air, easily soluble in water, and the aqueous solution has an acid reaction. The sulphates of the alkalies and of the alkaline earths yield with cadmium sulphate well-crystallized double salts. It has been used as an astringent in diseases of the eye.

Cadmium Nitrate, $Cd(NO_3)_2.4H_2O$, is obtained by dissolving the metal in nitric acid. It crystallizes in fibrous needles, which are very deliquescent, and are, therefore, very soluble in water; soluble also in alcohol.

Cadmium Carbonate.—The normal salt $CdCO_3$ appears not to be known. The basic salt is obtained by precipitating solution of cadmium sulphate with sodium carbonate. It has a variable composition, and in other respects resembles the corresponding zinc salt.

Cadmium Sulphide, CdS, is obtained as a yellow powder, insoluble in hydrochloric acid. It is used as a pigment under the names of *King's yellow* and *jaune brillant.*

CHAPTER IV.

THE SILVER GROUP.

SILVER (Argentum).

Symbol, Ag. *Atomic Weight*, 107.66. *Valence*, 1.

History.—Silver was one of the earliest known metals. It was the *Luna* or *Diana* of the alchemists.

Occurrence.—Native silver is found to some extent; large masses have been found in Norway, in Peru, and in Western United States. In the Lake Superior district it occurs associated with copper, but not alloyed with it, which points to the fact that deposition has taken place from solution. In combination silver occurs most abundantly as sulphide, argentite, or silver glance, Ag_2S. In other minerals it is associated with lead, copper, antimony, gold, and mercury. The rarer minerals containing silver are the combinations of it with the halogens, chlorine, bromine, and iodine; the compound with chlorine is known as horn silver. Small quantities of silver occur in nearly all lead ores, and although the amount appears to be small, nevertheless the quantity extracted from this source is very considerable. Silver occurs in sea water, and in the ash of some land plants.

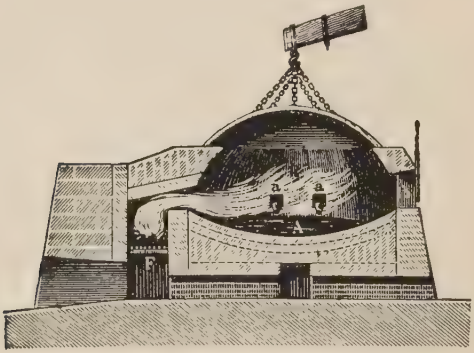
Extraction.—Metallic silver is extracted from its ores by several different processes, the most important of which are: (1) *The Cupellation Process*, (2) *The Amalgamation Process*, (3) *Extraction in the Wet Way*, (4) *Electrolytic Process.*

(1) *The Cupellation Process* is the oldest, and, with modifications to suit the ores in different localities, it is still in use. It is employed in the separation of silver from lead. When the lead is sufficiently rich in silver it is cupelled at once, but oftener it is necessary first to remove the large excess of lead; this is accomplished by the Pattinson process, which consists in melting the lead in an iron vessel and allowing it to cool slowly. Crystals of pure lead first separate, which are constantly removed by perforated ladles, and this is continued until but one-third of the metal in the pot remains. If then it is sufficiently rich in silver it is removed and cupelled. Instead of removing the excess of lead by Pattinson's process, the metal may be melted and zinc added in about the proportion of 18 parts of zinc for every 1 part of

silver present. The zinc alloys with the silver, rises to the top, and may be removed as a solid cake. This cake is then heated to redness in a current of air, by which the zinc is oxidized, and may be removed from the silver by washing with water.

The alloy of silver and lead obtained in the above processes is fused on the hearth of a reverberatory furnace, the bottom of which is covered with bone-ash or with a kind of clay. Such a furnace is shown in section in Fig. 128. *F* is the furnace, *A* the

FIG. 128.



Silver cupellation furnace, cross-section.

hearth, *a a* entrances for the blast of air, and *b* the working door. A rapid current of air is introduced over the molten metal on the hearth, by which the lead is oxidized, and either flows off through lateral openings or is skimmed off by workmen through the door *b*. Towards the end of the operation, the temperature is raised from a dark-red to a cherry-red heat, the surface of the metal is covered with iridescent films, but at last they disappear, and the metal then takes on the brilliant silver appearance known as *fulguration*. Fig. 129 shows an exterior view of the same furnace, *g* in this case being the working door, through which access is gained to skim the oxide from the metal.

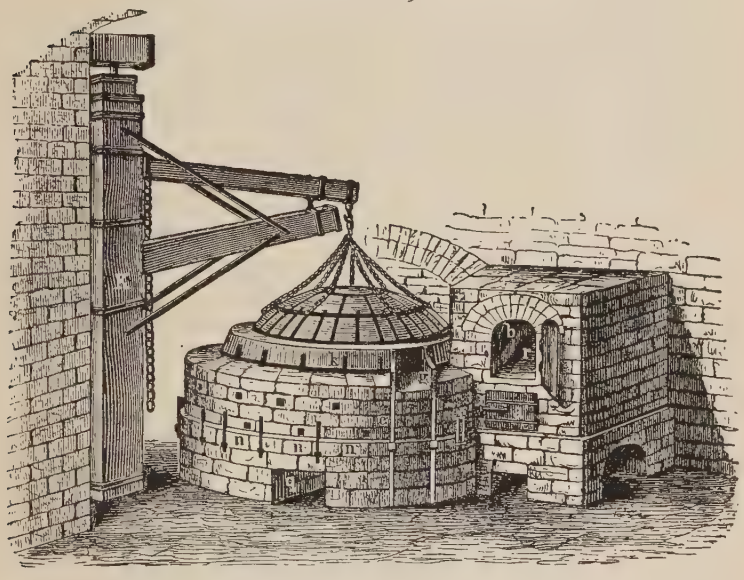
(2) *The Amalgamation Process* varies somewhat according to the locality in which it is conducted. That formerly employed at Freiberg consists in roasting the finely-ground ore with common salt, on the floor of a reverberatory furnace ; the mass is then again ground very fine, placed in a cask with scrap-iron and water, and agitated by machinery. The silver ore is converted into chloride in the roasting process, and this reacts when brought in contact with the iron as follows :

$$\underset{\text{Silver Chloride.}}{2AgCl} + \underset{\text{Iron.}}{Fe} = \underset{\text{Ferrous Chloride.}}{FeCl_2} + \underset{\text{Silver.}}{Ag_2}.$$

The silver is removed from the mass by further agitation with mercury, the liquid amalgam is strained off and subjected to distillation, which leaves the silver as a porous mass.

A modification of this method is employed in the United States, where it is known as the Washoe process, from the fact that it originated in the Washoe district of Nevada. The roasting process is frequently omitted, and the ore is intimately ground with common salt, copper sulphate, and mercury. Horses or mules are sometimes used in this operation. In order to over-

FIG. 129.



Silver cupellation furnace, exterior.

come the tendency of the mercury to remain in a minute state of subdivision termed *flouring* or *sickening*, it is frequently first amalgamated with about 2 per cent. of sodium, which prevents the formation of mercuric sulphide. The thoroughly ground, wet, and slimy mass is strained through bags, and the amalgam of silver and mercury is submitted to distillation, by which the silver is obtained as a residue.

The Mexican process is even more crude than the above, owing to the scarcity of water and fuel. The same mixture of ore,

water, common salt, copper sulphate, and mercury is used ; the mixing is almost invariably accomplished by mules, with intervals of allowing it to stand, so that from two weeks to two months are frequently required to effect the amalgamation of the silver.

(3) *Extraction in the Wet Way* is accomplished, according to Ziervogel's process, by roasting the ores, which usually contain sulphur, iron, and copper, at such a temperature that the sulphates of iron, copper, and silver, which are formed, are not all decomposed, but only the salts of iron and copper. The mass is then lixiviated with water, which dissolves the silver sulphate and leaves the insoluble oxides of iron and copper behind. The silver is removed from the solution by precipitation with metallic copper. A modification of this process consists in roasting with common salt, whereby silver chloride is formed, and is washed out from the mass by a solution of sodium thiosulphate ; from this solution the silver is precipitated as sulphide by sodium sulphide, and the silver sulphide is reduced to metal by heating to a high temperature in a current of air.

(4) *The Electrolytic Process.*—This method is used to separate silver from the native copper and copper oxide with which it occurs. The two poles, one of native copper oxide, CuO, and the other of native copper, are immersed in a bath of acid copper sulphate, and a strong current from a dynamo is sent through the solution, whereby the noble metals are dissolved from the copper oxide and deposited on the anode in powder.

Preparation of Pure Silver.—The metal obtained by the above processes is still contaminated with copper, and sometimes also with gold and platinum. To effect its purification, it is dissolved in nitric acid, which leaves gold undissolved, and from this filtered solution the silver is precipitated by hydrochloric acid. The washed and dried chloride is fused with an excess of sodium carbonate, and the pure metal collects at the bottom of the crucible.

Another method consists in reducing the chloride by laying it on plates of zinc and covering it with dilute hydrochloric acid. The metal is thereby obtained in a finely-divided state, in which form it has some uses in the laboratory.

Properties.—Silver is a pure white, lustrous metal, capable of taking a high polish. In some conditions, for instance, that in which it is obtained from some organic silver salts, it has a white, porcelain-like color, owing to the roughness of its surface, and is devoid of lustre.

The native silver is sometimes found in small crystals of the regular system. Of all the metals silver is the best conductor of heat and electricity. In hardness it stands between copper and gold. In malleability and ductility it is inferior only to gold; it has been beaten into leaf 0.00025 millimeter in thickness, and drawn into wire of such fineness that 180 metres weigh 0.1 gramme. In very thin films, as when deposited on glass from solution, it transmits blue light. Ordinarily the specific gravity of silver is 10.424, but when distilled it has a specific gravity of 10.575.

Silver fuses at a temperature of about 1040°, and at an intense white heat, such as is obtained from the oxyhydrogen lamp, it distils. When melted in air, pure silver absorbs 22 times its volume of oxygen, which it gives out again at the moment of solidification; this is sometimes accompanied with the projection of small particles of the metal, and is termed the *spitting of silver*.

When exposed to the atmosphere or to water, silver remains unchanged, but in the presence of a small quantity of ozone it becomes coated with a thin layer of oxide. The darkening, which sometimes takes place when silver is exposed to the air, is due to small quantities of hydrogen sulphide.

Nitric acid is the best solvent of silver. The compact metal is only slightly attacked by hydrochloric or dilute sulphuric acid even at the boiling temperature. In the presence of potassium permanganate the metal is dissolved by dilute sulphuric acid.

The finely-divided metal is slightly attacked by hydrochloric acid with evolution of hydrogen and formation of silver chloride; hydriodic acid acts more energetically upon it. Concentrated sulphuric acid dissolves silver with evolution of sulphur dioxide and formation of silver sulphate.

The alkalies have little or no action on silver; potassium or sodium hydrate may be fused with it, and fused potassium nitrate has but little action upon it.

Uses.—The pure metal is used to prepare the salts of silver, and in the manufacture of certain utensils for pharmaceutical and chemical purposes, as crucibles, dishes, wire, foil, etc. For many of the purposes to which silver is applied it is too soft to resist wear, and in order to increase its hardness it is alloyed with copper in various proportions. In the United States, France, Germany, and Austria the proportion of copper is 10 per cent., and such an alloy is used in those countries for coinage. In England the proportion employed is 7.5 per cent. of copper.

The term *fineness* applied to silver indicates the parts per thousand of pure silver in the alloy ; for instance, in this country silver coin is spoken of as "900 fine ;" that is, 90 per cent. silver and 10 per cent. copper.

Electroplating.—This is a process in which a thin layer of silver is deposited on metallic surfaces by electrolysis. The object to be coated must have a conducting surface, and is made the negative pole ; a bar of silver acts as the positive pole. These electrodes are placed in a solution of silver cyanide in an excess of potassium cyanide. If the object to be coated is properly cleaned, the silver will be deposited on it as a coherent layer ; at the same time cyanogen is liberated at the positive pole and dissolves the silver, thereby keeping the silvering solution of constant strength.

The silvering solution used in electroplating is made by dissolving 1 part of silver nitrate in 50 parts of distilled water and mixed with a solution of 5 parts of potassium cyanide in 20 parts of distilled water.

Silvering on Glass.—When alkaline solutions of silver salts are mixed with certain organic compounds like grape-sugar, Rochelle salt, etc., the silver is deposited on the surface of the vessel in which it is contained as a thin, coherent film. The following process will yield satisfactory results if the glass be first thoroughly cleaned with alkali, and then washed with distilled water :

Dissolve 7.8 grammes of silver nitrate in 60 c.c. of water, and divide the solution in two equal portions. Dissolve, also, 3.11 grammes of Rochelle salt in 1180 c.c. of water, and heat the solution to the boiling point. Add to it gradually (so as not to stop the ebullition) one of the portions of silver solution, boil some 10 minutes longer, cool, and decant the clear liquid. To the other half of the silver solution add just sufficient ammonia water to dissolve the precipitate which is first formed, or only leave a faint cloudiness ; then add 360 c.c. of water and filter. Equal portions of these two solutions, when mixed and poured on glass, will deposit a brilliant coating of silver in about 10 minutes, according to the temperature of the room. The coating of silver should then be well washed, dried, and varnished. Plating is also accomplished by a number of mechanical processes.

The production of silver for the year 1897 in the United States amounted to 56,117,000 troy ounces of domestic origin, valued at $33,557,966, and 39,325,000 ounces from foreign ores and bullion.

SILVER AND THE HALOGENS.

Silver Chloride, AgCl, is found native as kerargyrite, or horn silver, in Mexico, Peru, Chili, and in various parts of Germany. It occurs in crystals of the regular system or in pearl-gray, translucent, wax-like masses. Sea water contains a small quantity of silver chloride.

Preparation.—Pure silver chloride is prepared by precipitating a solution of silver nitrate with pure hydrochloric acid. The precipitate is of a more or less cheesy consistence, but boiling or long standing causes it to become more granular; it is collected and washed until the washings cease to have an acid reaction. The whole process should be conducted with exclusion of light.

Properties.—The artificially-prepared salt is a white, amorphous, insoluble powder. The insolubility in water and dilute acids is so complete as to make the chloride the best salt by which to determine silver quantitatively. When freshly prepared, it is readily soluble in ammonium hydrate, in solutions of sodium thiosulphate, potassium cyanide, and concentrated mercuric and mercurous nitrate. On the application of heat, silver chloride melts at 260° to a thick, yellow liquid, which becomes a tough, solid mass on cooling. When exposed to light the salt rapidly darkens, with loss of chlorine. Dry silver chloride absorbs at ordinary temperatures 19 per cent. of its weight of gaseous ammonia, forming the ammonio-silver chloride, $AgCl,2NH_3$, a white compound, which at 37.7° gives off the ammonia.

Use.—Silver chloride finds some use in photography.

Silver Bromide, AgBr, occurs native as bromargyrite in Mexico and Chili. The bromide is prepared similarly to the chloride, by precipitating silver nitrate with hydrobromic acid or potassium bromide. It has a faint yellow color, and has the solubilities and many of the properties of the chloride. It is not easily soluble, however, in ammonium hydrate, and the dry bromide does not absorb ammonia; an ammonio-silver bromide is formed by allowing the ammoniacal solution to stand for some time. Silver bromide is largely used in photography.

Silver Iodide, AgI. **Argenti Iodidum,** U. S. P.—This salt occurs native as the mineral iodargyrite, in Mexico, Chili, Spain, and Arizona, in the form of thin, slightly elastic, hexagonal tables.

Preparation.—Silver iodide may be prepared in a variety of ways, by direct union of the elements, by dissolving silver in

hydriodic acid, etc., but it is most readily and economically obtained by adding a solution of potassium iodide to one of silver nitrate, collecting, washing, and drying the precipitate without exposure to light. It should be preserved in dark amber-colored vials.

Properties.—Silver iodide is a heavy, yellowish, amorphous powder, without odor or taste. It is insoluble in water, dilute acids, or solution of ammonium carbonate ; soluble in 2500 parts of stronger ammonia water. It is also dissolved by an aqueous solution of potassium cyanide, and by a concentrated solution of potassium iodide.

On the application of heat, silver iodide melts at 400° to a dark-red liquid, which, on cooling, congeals to a soft, yellow, translucent mass. The dry precipitated compound absorbs 12.68 per cent. of ammonia gas, forming the white compound $AgI,2NH_3$, which on exposure to air gives off ammonia and becomes yellow.

Like the chloride and bromide, silver iodide has considerable use in photography. It also has some use in medicine, probably on account of the claim made that it does not discolor the skin like the other silver salts.

Silver Fluoride, AgF, is obtained by dissolving silver oxide or carbonate in hydrofluoric acid. It is a deliquescent salt, soluble in one-half its weight of water.

SILVER AND OXYGEN.

Silver Suboxide, Ag_4O, *Argentous Oxide*, is obtained by the action of hydrogen on certain salts of silver, preferably the citrate. This has a dark, metallic lustre, and decomposes on heating into oxygen and silver.

Silver Oxide, Ag_2O. *Argentic Oxide*, **Argenti Oxidum**, U. S. P.—A solution of 10 parts of silver nitrate in 100 parts of water is treated with solution of sodium hydrate so long as a precipitate is formed :

$$\underset{\text{Silver Nitrate.}}{2AgNO_3} + \underset{\text{Sodium Hydrate.}}{2NaOH} = \underset{\text{Silver Oxide.}}{Ag_2O} + \underset{\text{Sodium Nitrate.}}{2NaNO_3} + \underset{\text{Water.}}{H_2O}.$$

The precipitate is first washed by decantation, then on a filter, until the washings cease to give a reaction for nitric acid, and finally dried in the dark at ordinary temperatures.

Properties.—Silver oxide is a heavy, dark-brown or black powder, according to the method of preparation ; the darker product is obtained when precipitation has taken place from hot concentrated solutions, or when the drying has been conducted

at temperatures at or above 70°. It is slightly soluble in water, to which it imparts an alkaline reaction, insoluble in alcohol, and completely soluble in nitric acid without effervescence. When heated to 250° or 300°, it is decomposed into metallic silver and oxygen.

In the freshly-precipitated, moist condition silver oxide is more active than the same compound after it has been dried and then moistened. In the freshly-precipitated state it decomposes soluble chlorides, precipitates oxides from many metallic salts, and absorbs carbon dioxide from the air.

Silver oxide should not be triturated with antimony sulphide, arsenic sulphide, precipitated sulphur, amorphous phosphorus, tannin, or other easily oxidizable substances, since such mixtures readily inflame. Silver oxide is soluble in concentrated solution of ammonia, and on diluting this solution with water, black crystals of *ammonio-silver oxide* (Berthollet's fulminating silver) separate; these on drying become very explosive; for this reason the precaution should be observed not to bring silver oxide in contact with ammonia.

Silver oxide has some use in medicine, but its greatest value is as a laboratory reagent, where it is employed in the freshly-precipitated condition.

Silver Peroxide, Ag_2O_2, is also known, having been obtained by electrolysis of the nitrate in solution.

OXYGEN SALTS OF SILVER.

Silver Chlorate, $AgClO_3$, is prepared by dissolving silver oxide in chloric acid. It forms small, quadratic crystals, soluble in 10 parts of water.

Silver Bromate, $AgBrO_3$, and *Silver Iodate*, $AgIO_3$, are difficultly soluble, white, crystalline precipitates, obtained by treating solution of silver nitrate with potassium bromate or iodate.

Silver Sulphite, Ag_2SO_3, is obtained as a white, cheesy precipitate when sulphurous acid is added to a solution of silver nitrate.

Silver Sulphate, Ag_2SO_4, is prepared by dissolving silver in concentrated sulphuric acid, or by adding sulphuric acid to an alcoholic solution of silver nitrate.

It forms in small, lustrous, rhombic crystals, which are isomorphous with anhydrous sodium sulphate. It is soluble in 200 parts of cold water and in 70 parts of boiling water; insoluble in alcohol.

Silver sulphate is obtained in considerable quantities in the commercial separation of silver from gold by means of sulphuric acid, and is used to furnish pure silver.

Acid Silver Sulphate, $AgHSO_4$, is formed by dissolving silver sulphate in hot, concentrated sulphuric acid, and allowing the solution to cool.

Silver Pyrosulphate, $Ag_2S_2O_7$, results when silver sulphate is heated with sulphur trioxide.

Silver Thiosulphate, $Ag_2S_2O_3$, is also known.

Silver Nitrite, $AgNO_2$.—On mixing warm, concentrated solutions of 16 parts of silver nitrate and 10 parts of potassium nitrite, a crystalline precipitate of silver nitrite results.

Silver Nitrate, $AgNO_3$. **Argenti Nitras**, U. S. P.—This salt was first obtained in the crystalline form by Geber, in the eighth century. It came into medical use in the seventeenth century, under the names of *magisterium argenti*, *crystalli dianæ*, and when cast into sticks as *lapis infernalis* and *lunar caustic*.

A pure silver should be selected for the preparation of the nitrate ; that made from the sulphate answers this purpose very well. In a capacious porcelain dish 3 parts of metallic silver are mixed with 10 parts of nitric acid (containing 25 per cent. HNO_3), and the mixture warmed until the reaction begins. In case the silver is finely divided, the action is sufficiently active without warming, and may have to be controlled by the addition of a little cold water :

$$3Ag + 4HNO_3 = 3AgNO_3 + 2H_2O + NO.$$

A funnel should be inverted over the liquid in the dish to prevent particles of the acid and solution from flying out, and when the action ceases, the silver being dissolved, the sides of the funnel are rinsed down with distilled water ; the solution is filtered through glass wool, if necessary, and evaporated on a sand-bath to dryness. The temperature is then raised so as to melt the salt and complete the escape of nitrous fumes, which is soon accomplished when the salt is pure ; but when it contains copper nitrate it takes somewhat longer, and the copper is converted into insoluble oxide, as follows :

$$Cu(NO_3)_2 = CuO + 2NO_2 + O.$$

The reaction is known to be ended when there is no further evolution of gas, and the mass becomes dark or black from the formation of the copper oxide.

The fused mass is dissolved in double its weight of water, filtered through a small, well-washed filter, and set aside to crystallize ; dust and light should be excluded as far as possible during the operation. In case lunar caustic is wanted, the fused silver nitrate is treated with a few drops of nitric acid to oxidize any nitrite, and after a few moments more heating, is poured into polished iron moulds such as are used in the preparation of sticks

of sodium or potassium hydrate; see Fig. 114, p. 359. It is preferable to have such moulds gold-plated.

Properties.—Silver nitrate occurs in colorless, transparent, tabular, rhombic crystals, permanent in the air, but becoming gray or grayish-black on exposure to light in the presence of organic matter. It is without odor, but has a bitter, caustic, and metallic taste.

The salt is soluble in 0.6 part of water at 15°, and in 0.1 part of boiling water; also soluble in 26 parts of cold and in 5 parts of boiling alcohol.

On the application of heat, the salt melts at about 200° without decomposition, and on cooling forms a white, crystalline mass. If kept for some time at a temperature above 210° it begins to decompose with formation of silver oxide and silver nitrite. At a red heat decomposition takes place, nitrous fumes, nitrogen, and oxygen being evolved and metallic silver remaining. The aqueous solution of silver nitrate is neutral to litmus.

Solution of ammonia added to a solution of silver nitrate at first produces a precipitate which in the presence of a larger amount of the reagent dissolves; if this solution then be allowed to evaporate, rhombic, prismatic crystals separate, having the composition $AgNO_3, 2NH_3$. When heated above 100° they melt, evolving nitrogen and ammonia, leaving a residue of ammonium nitrate and a mirror of metallic silver.

Uses.—Silver nitrate is largely used as a laboratory reagent and in photography. It also has considerable use in medicine as a cautery, its employment internally being limited; when used internally for some time it produces a peculiar bronze coloration of the skin.

For external use there are two preparations of silver: **Argenti Nitras Fusus,** U. S. P., and **Argenti Nitras Dilutus,** U. S. P., which are usually employed. The fused nitrate, or *lunar caustic*, contains a small quantity of silver chloride in order to toughen it; this is accomplished by adding to 100 grammes of the salt 4 grammes of hydrochloric acid, melting the mixture at as low a temperature as possible, and pouring into suitable moulds. The diluted silver nitrate, or *mitigated caustic*, is made by melting at the lowest possible temperature 30 grammes of silver nitrate and 60 grammes of potassium nitrate, and casting in suitable moulds.

Silver Phosphate, Ag_3PO_4, is obtained when the normal sodium phosphate or the disodium hydrogen phosphate is added to a solution of silver nitrate. It is a yellow, amorphous compound, insoluble in water.

Compounds of silver with pyrophosphoric acid and with metaphosphoric acid are also known.

Silver Carbonate, Ag_2CO_3, is obtained by adding sodium carbonate to silver nitrate solution, collecting and washing the precipitate. It is a yellow, amorphous powder, insoluble in water.

Silver Sulphide, Ag_2S, is found native as argentite or vitreous silver, in grayish-black crystals of the regular system. It can be obtained artificially by igniting silver chloride in a current of hydrogen sulphide.

Much of the so-called *oxidized silver* is coated with a thin layer of sulphide, obtained by heating together silver and solution of potassium sulphide. A more permanent result is obtained by coating the silver with platinic chloride solution. In both cases considerable washing and polishing are necessary to get a good result.

GOLD (Aurum).

Symbol, Au. *Atomic Weight*, 196.7. *Valence*, I and III.

History.—Gold has been known from the earliest times. On account of its scarcity, its color, and its stability in contact with air, it early became an important metal from which to make jewelry, certain household utensils, and money.

Occurrence.—Gold is very widely distributed in nature, but always in small quantities. It is ordinarily found in the free or uncombined state; rarely it is found amalgamated with mercury or combined with tellurium.

In the free state it is frequently in a crystalline condition, the commonest forms being the octohedron or tetrahedron; occasionally the elongated forms of these give it the appearance of being acicular.

The native deposits are usually in veins of quartz, although the usual source of the metal is in alluvial soils resulting from the disintegration of the rocks in which it was imbedded. It is found in the sand of most rivers and in sea water.

Gold is rarely found in a pure condition, it being usually mixed with silver, and more rarely with copper, iron, and platinum; when it contains more than 36 per cent. of silver it is termed *electrum*.

The principal localities in which gold is found in sufficient quantity to extract are the gold-fields of Western United States, Alaska, Australia, Siberia, Transylvania, Brazil, New Zealand, and South Africa.

The United States in 1897 produced 2,685,000 troy ounces, valued at $55,498,950. This was not far from 23 per cent. of the output of the whole world.

Extraction.—Most of the gold is obtained by a process of levigation, in which sand and alluvial deposit from gold-bearing rocks are washed with water, the lighter portions being allowed to run off, while the heavier portions with the gold remain and are intimately mixed with mercury, so that an amalgam of gold and mercury is formed, from which the latter is distilled. This is a very brief outline of the process, which has innumerable modifications; for instance, it may be carried out by one man with a pan, when it is termed *pan-washing;* or a little more elaborate apparatus may be employed, requiring the attention of four men, when it is termed *cradle-washing;* or, finally, *hydraulic mining* may be used. The last consists in washing large quantities of earth by means of water brought from higher situations in the mountains, so that enormous quantities may be employed. The water and earth are run through a long series of troughs, cut in the rock, and in these troughs depressions are cut at intervals termed "sluice-boxes," in which small quantities of mercury are placed, so that the gold is taken out by it. In addition to the boxes, plates of copper coated with mercury are often placed in the troughs to arrest the finer particles of gold; these plates are removed from time to time, the surface scraped, and, after re-amalgamation, returned.

When quartz rock is worked, it is first reduced to a fine powder by mechanical processes, and then washed.

The *chlorine process* is sometimes used, especially where the metal is associated with pyrites. The ore is first roasted, then mixed with water in tubs, and saturated with chlorine; this is allowed to stand 10 to 12 hours, when the gold passes into solution; the solution containing gold chloride is run off and treated with ferrous sulphate, which precipitates the metallic gold in the form of a fine powder, which is collected and fused to a globule with borax.

The *cyanide process* consists in leaching the finely comminuted ore with a very dilute solution of potassium or sodium cyanide, which, in the presence of oxygen, reacts with the gold to form a soluble double cyanide of gold and potassium. The gold is precipitated from the solution by means of metallic zinc or the electric current. The details of the process require modification for the various ores.

Gold prepared by the above processes contains silver, copper, or platinum,—sometimes all three. When the proportion of gold does not exceed 33 per cent. the silver of the alloy may be dissolved by nitric acid of specific gravity 1.320; this was formerly known as *quartation*, because it was believed that an alloy must not contain over 25 per cent. gold in order for the silver to be dissolved by the acid. When the gold in the alloy exceeds 33 per cent. it is fused with sufficient silver to reduce it to that proportion, when the silver can be removed by nitric acid. Sulphuric acid is used in the same way to separate gold. An alloy may contain 25 per cent. gold and 10 per cent. copper; the acid should have a specific gravity of 1.840.

When a sample of gold does not contain more than 10 per cent. of silver, it is fused in a clay crucible, which has been glazed on the inside with borax, and a stream of chlorine is passed into the molten metal; silver chloride forms and rises to the top, a layer of borax prevents it

from volatilizing; the chlorides of zinc, bismuth, arsenic, and antimony, when present, are volatilized. A final purification is sometimes given to the gold, after removal of silver, by dissolving it in nitrohydrochloric acid, evaporating on a water-bath to a syrupy consistence, mixing this with some 20 times its volume of water, filtering, and treating the filtrate with solution of ferrous chloride, when metallic gold is precipitated according to the following reaction:

$2AuCl_3$	+	$6FeCl_2$	=	$2Au$	+	$3Fe_2Cl_6$.
Gold Chloride.		Ferrous Chloride.		Gold.		Ferric Chloride.

Oxalic acid or ferrous sulphate may be used to effect this precipitation of the gold.

Properties.—In the compact state gold has a characteristic yellow color, a peculiar lustre, and is capable of a high polish. In the precipitated condition it is a brown powder. The native gold occurs in small cubical or octohedral crystals, and sometimes in other forms of the regular system. It is the most malleable and ductile of the metals; in very thin leaves it transmits a green light. When pure it is nearly as soft as lead. The specific gravity varies, according to its mode of preparation or treatment, from 19.26 to 19.55. On the application of heat it melts at 1240° to a bluish-green liquid.

Gold is not affected at any temperature by air, oxygen, or water. It is not dissolved by any of the acids singly, unless it be selenic acid. It is dissolved by nitrohydrochloric acid, free chlorine, and bromine, and in a lesser degree by iodine. It is also attacked by the fused alkalies and fused potassium nitrate.

Uses.—Gold is used for coinage, for jewelry, and for gilding; gold leaf is employed in the latter process, while the finely-precipitated gold is used in the decoration of glass and porcelain. Gilding is oftener accomplished now by electrolytic deposition; solutions of gold chloride and potassium cyanide constitute the bath, and a piece of gold plate is employed as the positive pole.

Alloys.—Pure gold is too soft for most purposes, and is therefore alloyed with silver or copper; the latter metal gives it a reddish color. When pure it is designated as 24-carat, or 1000 fine. In England the coinage is 22-carat, equivalent to a fineness of 916.66; in most other European countries and in the United States it is 21.6-carat, or 900 fine.

Alloys for jewelry contain both silver and copper; that of 14-carat is, perhaps, used the most extensively.

GOLD AND THE HALOGENS.

The halogen elements combine with gold in two proportions, in which the metal acts with the equivalence I and III; for example, AuCl and $AuCl_3$.

Aurous Chloride, AuCl, *Gold Monochloride*, is obtained as a yellow powder by carefully heating auric chloride to 185° ; it is decomposed at higher temperatures into gold and chlorine. Water decomposes it into the metal and auric chloride.

Aurous Bromide, AuBr, and *Aurous Iodide*, AuI, are known.

Auric Chloride, $AuCl_3$. *Gold Trichloride.*—This compound is prepared by dissolving gold in nitrohydrochloric acid, evaporating to dryness, dissolving in water, and again evaporating to dryness ; on now heating this residue carefully to 150°, the anhydrous salt is obtained. The salt may also be prepared by heating gold leaf in a current of chlorine at a temperature of 180° to 190°, when it sublimes in reddish crystals. Although gold chloride is decomposed at 185°, as above stated, yet, in a current of chlorine, it may be sublimed at a temperature of 300° without decomposition.

When the hot, concentrated solution of gold chloride is allowed to cool, crystals having the composition $AuCl_3.2H_2O$ are deposited.

Auric chloride forms numerous double compounds with other chlorides and with hydrochloric acid.

Chlor-auric Acid, $AuCl_3,HCl.4H_2O$, is one of the double compounds with hydrochloric acid. It is formed when hydrochloric acid is added to a solution of auric chloride, and the whole is allowed to evaporate slowly over quick-lime ; long, yellow crystals are deposited, which rapidly deliquesce on exposure to the air. This compound forms a series of salts termed *chlor-aurates*, or they may simply be considered double compounds of auric chloride with the salt ; the best known of these is *sodium chloraurate*, or *gold* and *sodium chloride*. This compound is prepared by dissolving gold in a mixture of nitric and hydrochloric acids, and evaporating the solution on a water-bath to a syrupy consistence :

$2Au$	$+$	$8HCl$	$+$	$2HNO_3$	$=$	$2AuCl_3,HCl$	$+$	$2NO$	$+$	$4H_2O.$
Gold.		Hydrochloric Acid.		Nitric Acid.		Chlor-auric Acid.		Nitric Oxide.		Water.

The proportions are 10 parts of gold to 13 parts of nitric acid of 25 per cent., and 32 parts of hydrochloric acid of 25 per cent. The syrupy solution of chlor-auric acid is treated with a solution of 4 parts of pure sodium chloride in 60 parts of water, and the resulting mixture evaporated until a pellicle forms ; evaporation being completed at ordinary temperatures over quick-lime :

$AuCl_3,HCl$	$+$	$NaCl$	$=$	$AuCl_3,NaCl$	$+$	$HCl.$
Chlor-auric Acid.		Sodium Chloride.		Gold and Sodium Chloride.		Hydrochloric Acid.

The **Auri et Sodii Chloridum,** U. S. P., is a mixture prepared by rubbing together equal parts of dry gold chloride and sodium chloride. Theoretically it contains 32 per cent. of metallic gold, although the official requirements are simply that it shall contain not less than 30 per cent. of this metal.

The true gold and sodium chloride has the formula $AuCl_3$,-$NaCl.2H_2O$, and contains 49.5 per cent. of metallic gold. It occurs in orange-yellow, rhombic tables or prisms, is deliquescent, and when exposed to a red heat decomposes, leaving a residue of metallic gold.

This compound is used in photography, for gilding, and to some extent in medicine.

Auric Bromide, $AuBr_3$ (Gold Tribromide), *Auric Dibromide*, $AuBr_2$, and *Auric Iodide*, AuI_3, are known.

GOLD AND OXYGEN.

Aurous Oxide, Au_2O, is a dark-violet powder, obtained by treating aurous chloride with potassium hydrate in the cold.

Auric Oxide, Au_2O_3, is a dark-brown powder, formed by heating auric hydrate to 100°. Strong heat decomposes it into gold and oxygen.

Auric Hydrate, $Au(OH)_3$, *Gold Hydroxide*, *Auric Acid.*—This compound is best prepared by heating a solution of auric chloride with magnesia, and washing the precipitate with dilute nitric acid. When freshly prepared it is a yellowish-brown precipitate, which on drying becomes a brown powder. Auric hydrate is acid-forming, and its salts are termed aurates. When it is treated with an excess of ammonia water, a green to brown powder is formed, known as *fulminating gold.* In the dry state this ammonia compound explodes violently, either by percussion or on heating.

AURATES.

Potassium Aurate, $KAuO_2.3H_2O$, is the only one of these compounds that has been investigated. It is obtained by dissolving auric hydrate in potassium hydrate solution, and evaporating the resulting solution in a vacuum. It forms in small, yellow, acicular crystals, which are readily soluble in water and have a strong alkaline reaction. It is used in gilding copper and some other metals.

CHAPTER V.

THE COPPER AND MERCURY GROUP.

COPPER.

Symbol, Cu. *Atomic Weight*, 63.18. *Valence*, $(R_2)^{II}$ and II.

History.—Copper, because of its rather abundant occurrence in the metallic state, was probably the first metal used by man. It formed the material for tools and weapons before the metallurgical processes necessary to produce iron were known. Originally copper was found in the island of Cyprus, and on this account its name gradually came to be *cuprum*.

Occurrence.—The most abundant occurrence of native copper is in the State of Michigan, in what is known as the Lake Superior district. Valuable ores of copper are found in Cornwall, England, in Siberia, and in the Ural. Spain, Chili, Peru, Japan, and Australia also produce considerable quantities. One of the most abundant ores of copper is cuprous oxide, Cu_2O, or red copper ore ; cupric oxide, CuO, is found more rarely. The sulphide, or copper glance, Cu_2S, is also widely distributed. Smaller quantities occur as malachite, or copper carbonate, $CuCO_3,Cu(OH)_2$. Bornite and chalcopyrite are mixed sulphides of copper and iron, and are very widely distributed.

Extraction.—The method of obtaining copper from its ores depends on whether the ore is an oxide or sulphide. If an oxide or a carbonate, the ore is simply heated with charcoal or other fuel, with, perhaps, the addition of some flux rich in silica. This process is much employed in the United States. Usually, however, the ore is a sulphide mixed with iron sulphide, lead, antimony, and silver ; often not more than 13 per cent. of copper is present. The ore is first roasted on the floor of a reverberatory furnace, the air-supply being controlled by suitable apertures. In this way the sulphides are partly converted into oxides. The roasted ore is next fused with a silicious flux, to which fluor-spar is sometimes added to increase its fusibility. The temperature for this operation is much higher than that required in the roasting process. The result of this operation is cuprous sulphide and a slag formed by combination of the iron oxide present with the flux. The cuprous sulphide, with some unaltered iron sulphide,

collects in the basin of the furnace and is known as coarse metal. This operation of fusing with a flux is repeated until the iron is entirely removed, and a mixture of cuprous oxide and sulphide remains. On roasting this mixture the following reaction takes place:

$$\underset{\text{Cuprous Oxide.}}{2Cu_2O} + \underset{\text{Cuprous Sulphide.}}{Cu_2S} = \underset{\text{Copper.}}{6Cu} + \underset{\text{Sulphur Dioxide.}}{SO_2}.$$

The copper thus obtained is usually covered with black blisters, and is known as *blister copper*. It still contains impurities of lead, antimony, arsenic, and occasionally other metals, which are removed by another treatment in a current of air; the impurities, with some of the copper, form a slag with the silicious material of the hearth and are removed. This slag is known as refinery slag, and is used as a flux during the earlier treatments of the ore. The metal still contains some cuprous oxide, which renders it brittle, so it must be subjected to a refining process which is known as *poling*, because it consists in melting the copper with coal, and stirring the melted mass with an oak or birch pole; the gases evolved complete the deoxidation of the metal; the latter is then run into ingots.

The most recent process of copper refining is that in which electrolysis is employed. Both copper sulphate and chloride are taken in solution for electrolysis.

It is estimated that the United States now produces over 80,000 tons of refined copper electrolytically from blister copper.

Considerable quantities of copper are now obtained by extraction in the wet way. The residue from the burning of iron pyrites, in the manufacture of sulphuric acid, contains about 3 per cent. of copper. This is recovered by roasting the residue with 12 to 15 per cent. of common salt. On lixiviating this mass with water, the whole of the copper is obtained as cupric chloride, and is precipitated from the solution by the addition of scrap-iron.

Properties. — Copper is a lustrous, malleable, and ductile metal, with a peculiar reddish color, and capable of taking a high polish. Its specific gravity is about 8.94, and it melts between 1200° and 1300°. In the molten state it possesses a bluish-green color. Native copper is found crystallized in octohedrons, and occasionally in the same form it occurs in the refining process.

In dry air copper undergoes no change, but in the presence of moisture it becomes covered with a greenish layer of basic copper

carbonate. When heated in air or oxygen the metal becomes black on the surface, owing to the formation of a thin layer of oxide.

With exclusion of air, copper is scarcely dissolved by dilute hydrochloric or sulphuric acid; on the application of heat and in the presence of air, however, either will slowly dissolve it. Dilute nitric acid readily dissolves it in the cold. It is also dissolved by ammonia water in the presence of air.

Uses.—Metallic copper is used for making many kinds of metals for manufacturing and domestic purposes, for sheathing ships, in the manufacture of money, in cartridge-shells, and especially in alloys.

The total production of copper in the United States for 1897 amounted to 475,338,340 pounds, valued at $52,478,352. Of this amount 60.5 per cent. was exported.

Alloys of Copper.—The most important alloys of copper are those it forms with zinc and tin.

Brass is composed of about 70 per cent. copper and 30 per cent. zinc, with sometimes 2 or 3 per cent. of tin and 0.25 to 0.80 per cent. of lead. Brass is superior to copper because it does not tarnish so readily, it has a more pleasing color, is harder, has a lower melting point, and when cast does not blister. *Pinchbeck*, or *tombak*, is a brass containing 85 parts copper and 15 parts zinc.

The following are the percentages in some of the other important alloys of copper:

	Copper.	Tin.	Lead.
Bell metal	78	22	. .
Gun metal	90	9	. .
Art bronze	86.6	6.6	3.3

COPPER AND THE HALOGENS.

Cuprous Chloride, Cu_2Cl_2, is formed by dissolving cuprous oxide in hydrochloric acid, taking care to exclude air. It is probably most readily prepared by boiling cupric chloride with hydrochloric acid and copper turnings, with the addition of a little platinic chloride to establish galvanic action. On pouring the clear solution into water, which has been heated to expel air, cuprous chloride separates as a white, crystalline precipitate of microscopic tetrahedra.

Properties.—Cuprous chloride is a white, crystalline powder, which may be recrystallized by dissolving in hot, concentrated hydrochloric acid; it is insoluble in water, but is soluble in solution of ammonia.

On the application of heat cuprous chloride melts at 434°, and on cooling it forms a solid, crystalline mass. Near 1000° it is volatilized, and the vapor has a specific gravity of 6.83 (air = 1), indicating the formula Cu_2Cl_2.

The solution of cuprous chloride in hydrochloric acid and in ammonia possesses a strong affinity for carbon monoxide, and for a number of compounds of the acetylene series; it is, therefore, a valuable agent in gas analysis.

Cupric Chloride, $CuCl_2.2H_2O$, is prepared by dissolving 1 part of cupric oxide in 4 parts of hydrochloric acid of 25-per-cent. strength. The solution is filtered clear, concentrated on a water-bath, and crystallized.

Properties.—Cupric chloride occurs in green, prismatic crystals, which deliquesce on exposure to damp air. It is readily soluble in water and in alcohol, and somewhat soluble in ether. The aqueous solution of the salt is green when concentrated, and blue when dilute.

At 100° the crystals begin to lose their water of crystallization, and at 500° the salt melts; when heated to redness it is decomposed into cuprous chloride and chlorine.

The anhydrous cupric chloride readily absorbs ammonia and becomes thereby converted into a blue powder, having the composition $CuCl_2,6NH_3$. The solution of the salt in strong aqueous ammonia deposits octohedral crystals of the composition $CuCl_2,4NH_3.H_2O$. Both of the above compounds are changed at 150° into a green powder, having the composition $CuCl_2,2NH_3$.

When cupric chloride solution is digested with cupric hydrate, or when potassium hydrate is added to a cupric chloride solution, there is formed a compound having the composition $Cu_4O_3Cl_2.4H_2O$, and known as atacamite. This mineral occurs native in Chili and Peru.

Cuprous Bromide, Cu_2Br_2, and *Cupric Bromide*, $CuBr_2$, are prepared like the corresponding chlorides, and resemble them in appearance and properties. The anhydrous cupric bromide occurs in lustrous crystals resembling iodine.

Cuprous Iodide, Cu_2I_2, is the only compound of copper and iodine known; it is a white, permanent, insoluble powder, which is prepared by adding potassium iodide to copper sulphate in the presence of sulphurous acid or ferrous sulphate:

$$2CuSO_4 + 2KI + 2FeSO_4 = Cu_2I_2 + K_2SO_4 + Fe_2(SO_4)_3.$$

Iodine is frequently separated from bromine and chlorine by this reaction.

Cuprous Fluoride, Cu_2F_2, and *Cupric Fluoride*, CuF_2, are known; the latter may be made to crystallize with two molecules of water.

COPPER AND OXYGEN.

Cuprous Oxide, Cu_2O.—This compound is found native as cuprite, or red copper ore, in regular octohedrons or compact crystalline masses. It is readily prepared by fusing cuprous chloride with anhydrous sodium carbonate, or by heating solutions of copper sulphate, sodium hydrate, and sugar. It is a red powder, wholly insoluble in water, but soluble in solution of ammonia. It is used as a red coloring for glass.

Cupric Oxide, CuO, occurs native as black oxide of copper or melaconite in dark, earthy masses, or rarely in cubes. It is artificially prepared

by heating to redness copper nitrate or oxycarbonate, or by heating metallic copper to redness with access of air.

Properties.—Cupric oxide is a fine, amorphous, brownish-black powder; sometimes it is found in scales. It is insoluble in water, but easily dissolves in acids with the formation of cupric salts; it is also soluble in solution of ammonia.

When heated in the presence of hydrogen, carbon monoxide, marsh-gas, and many other organic substances, cupric oxide readily gives up its oxygen and is reduced to metallic copper. On account of this property it is much employed in organic analysis.

When fused with glass it imparts to the latter a light-green color; it is, therefore, employed in the preparation of artificial emeralds.

Cuprous Hydrate, $Cu_2(OH)_2$, having this formula, is not known, but a compound derived from it, having the composition $4Cu_2O.H_2O$, is made by pouring a solution of cuprous chloride into a cold solution of sodium hydrate. It is a bright yellow precipitate. It readily passes into cuprous oxide on the application of a gentle heat, and on exposure to air becomes blue by oxidation.

Cupric Hydrate, $Cu(OH)_2$, is readily obtained as a light-blue, bulky precipitate, when a solution of copper sulphate is treated in the cold with excess of sodium hydrate. When this mixture is boiled, the hydrate is converted into a black compound having the composition $Cu(OH)_2.2CuO$, and this, when dried and ignited, is converted into CuO.

At least two other oxides of copper are known,—namely, Cu_4O, copper tetroxide, and copper superoxide or dioxide, $CuO_2.H_2O$.

OXYGEN SALTS OF COPPER.

Cupric Sulphate, $CuSO_4.5H_2O$. **Cupri Sulphas, U. S. P.**—This salt is most readily prepared by dissolving copper in sulphuric acid:

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$

The clear solution is decanted and allowed to crystallize, and these crystals are further purified by recrystallization. Copper sulphate is a by-product in several metallurgical operations, so that its preparation is usually carried on in conjunction with them. The crude copper obtained in smelting the ores is treated with sulphuric acid, and thus converted into sulphate. Copper pyrites are roasted, when the following reaction takes place:

$$Cu_2S + 5O = CuSO_4 + CuO.$$

This mixture is then treated with so much sulphuric acid as is necessary to convert the oxide into sulphate.

Large quantities of copper sulphate are obtained in the refining of silver when that metal contains copper and gold. Silver and copper sulphates are formed, and from their solution the silver is

precipitated by suspending in the liquid strips of copper. Commercial copper sulphate frequently contains small quantities of iron and zinc salts. *Double vitriol*, for which at one time there was some demand, consists of the sulphates of copper and iron, with occasionally some zinc sulphate.

Properties.—Copper sulphate occurs in "large, transparent, deep blue, triclinic crystals, odorless, of a nauseous, metallic taste; slowly efflorescent in dry air." It is soluble in 2.6 parts of water at 15°, and in 0.5 part of boiling water; insoluble in alcohol. "When carefully and continuously heated to 30°, the salt loses 2 of its 5 molecules of water (14.43 per cent.), and is converted into a pale blue, amorphous powder. Two more molecules of water are lost at 100°, while the fifth is retained until 200° is exceeded, when a white, anhydrous powder remains (63.9 per cent. of the original weight). At a still higher temperature sulphur dioxide and oxygen are given off, and a residue of black cupric oxide is left."

The aqueous solution shows an acid reaction towards litmus paper.

Copper sulphate in a crystallized, anhydrous condition may be obtained by acting on copper in closed vessels with concentrated sulphuric acid. The salt in the anhydrous as well as in the hydrated condition has a strong affinity for hydrochloric acid, forming cupric chloride and liberating sulphuric acid; on account of this property copper sulphate is useful to separate hydrochloric acid from its mixture with other gases.

Copper sulphate is used in the manufacture of colors for calico-printing, as a mordant, and in electrotyping; it also is extensively employed in some galvanic batteries.

A number of basic compounds of copper and sulphuric acid are known, one of these, $CuSO_4,3Cu(OH)_2$, occurs in nature as the mineral brochantite.

Copper Ammonium Sulphate, $CuSO_4,4NH_3.H_2O$.—Several compounds of copper and ammonium sulphate exist. One, having the above formula, is produced in solution when ammonia water is added in excess to a solution of copper sulphate. It was official in the Pharmacopœia of 1870, and was prepared in the solid state by rubbing together, in a mortar, copper sulphate and ammonium carbonate, and drying the product between folds of bibulous paper. It occurs as a deep-blue, crystalline powder. Anhydrous copper sulphate absorbs gaseous ammonia with great avidity, forming the compound $CuSO_4,5NH_3$.

Copper Nitrate, $Cu(NO_3)_2.3H_2O$, *Cupric Nitrate*, is prepared by treating, in a capacious flask, 1 part of copper turnings with 11 parts of nitric acid of 25-per-cent. strength. The mixture is carefully warmed until the reaction begins, which then continues quietly without the further application of heat:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + N_2O_2 + 4H_2O.$$

The solution is diluted with water, filtered clear, and then evaporated until a film forms, when it is set aside to crystallize.

Properties.—Copper nitrate occurs in deep-blue, prismatic crystals; it possesses a sharp metallic taste, and is easily soluble in water and in alcohol. At low temperatures crystals are formed with 6 molecules of water. Like the sulphate, this salt forms an ammonia compound, having in this case the formula $Cu(NO_3)_2.4NH_3$.

Copper nitrate is used in dyeing and in calico-printing; it is also a convenient compound from which to prepare pure copper oxide.

Copper Phosphate, $Cu_3(PO_4)_2.3H_2O$, is formed when copper carbonate is dissolved in dilute phosphoric acid; on warming the solution to 70° the salt is deposited as a bluish-green, insoluble precipitate. Various compounds of copper and phosphoric acid are found in nature.

Copper Arsenite, $CuHAsO_3$, is known as *Scheele's green*, or *Swedish green*, and is obtained by mixing solutions of copper sulphate and potassium arsenite. *Paris green* is an aceto-arsenite of copper, and will be considered later.

Copper Arsenate, $Cu_3(AsO_4)_2.4H_2O$, is formed as an amorphous precipitate by warming equivalent quantities of copper nitrate and calcium arsenate with a little water to 60°. By varying the proportions of the above salts compounds of different composition may be obtained.

Copper Borate of variable composition is obtained by mixing solutions of copper sulphate and borax.

Copper Silicate, $CuSiO_3$, is found in nature with variable amounts of water. It may be obtained as a blue-green precipitate by mixing solutions of copper sulphate and sodium silicate.

Copper Carbonate.—The normal salt, $CuCO_3$, is not known, but a compound having the composition $CuCO_3,Cu(OH)_2$, is found in nature as the mineral malachite. Azurite, $2CuCO_3,Cu(OH)_2$, occurs with malachite and other copper ores.

Malachite occurs in the Urals, at Cornwall, England, and in various parts of the United States. It is susceptible of a high polish, and is on this account much used for making vases, ornamental table tops, and jewelry.

Azurite is sometimes known as blue malachite, and is employed in the same manner as the green variety.

When cold solutions of copper sulphate and sodium carbonate are mixed, a blue precipitate is thrown down having the composition $CuCO_3.Cu(OH)_2.H_2O$, which, on standing, becomes green, and has the same composition as malachite.

The term verdigris, or copper rust, is sometimes applied to the compound formed on copper when it is exposed to the joint action of air and water, and which has the same composition as malachite. The basic acetate of copper is usually understood as the true verdigris.

COPPER AND SULPHUR.

Cuprous Sulphide, Cu_2S, occurs native as the mineral *chalcocite*. It is formed when copper and sulphur are fused together, and has in this way been obtained in rhombic octohedrons.

Cupric Sulphide, CuS, when found in nature as the mineral *corellite*, is also known as indigo copper. It is formed as a black precipitate when hydrogen sulphide is passed into solution of copper sulphate. It is quite readily decomposed into cuprous sulphide and sulphur.

MERCURY (Hydrargyrum).

Symbol, Hg. *Atomic Weight*, 199.8. *Valence*, $(R_2)^{II}$ and II.

History.—Mercury, or quicksilver, was known to the ancients, but at a more recent period than gold and silver. It was first mentioned in the writings of Aristotle, 400 B.C., and in those of Theophrastus, 300 B.C. The latter described it as liquid silver, and gave a method for the preparation of it from cinnabar.

Occurrence.—Mercury is found native in minute globules disseminated through its ores. The most abundant ore is cinnabar, or mercuric sulphide, HgS. This is found at Idria, in Austro-Hungary; at Almaden, in Spain; in Nevada, Utah, and California, in the United States; in Mexico, New South Wales, China, and Japan.

The metal is also found amalgamated with gold and silver.

The production of mercury in the United States in 1897 amounted to 26,079 flasks (of 26½ pounds), valued at $991,002.

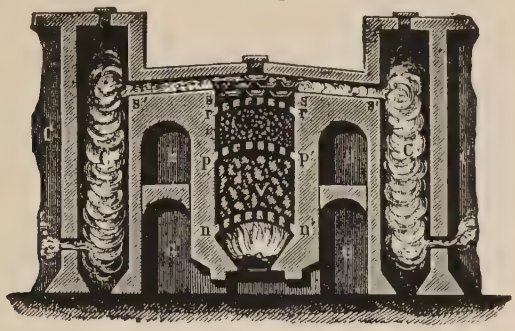
Preparation.—The chief ore of mercury being the sulphide, it is simply necessary to heat this ore to a temperature above 360° with access of air in order to decompose it into the metal and sulphur dioxide, as follows:

$$HgS + O_2 = Hg + SO_2.$$

The vapors are passed through a series of stone chambers, C C, Fig. 130, the last one of which is so arranged that water trickles down and meets the ascending column of vapor. The mercury collects under the water. This process is employed at Idria,

while at Almaden the vapors are conducted through a long series of vessels known as *aludels*, shown in Fig. 131. The combination between the mercury and sulphur is more easily destroyed in

FIG. 130.



Mercury furnace.

the presence of iron or lime, so that one of these is sometimes heated with the ore. When lime is employed the reaction is as follows :

$$4HgS + 4CaO = 4Hg + CaSO_4 + 3CaS.$$

In the United States these furnaces are usually so constructed as to be worked continuously, while in the older localities it is customary to allow the furnace to cool after each charge of about 50 tons has been heated ; this is usually accomplished in one day, and then four or five days are required for the cooling before

FIG. 131.

Aludels.

another charge can be filled in. Mercury prepared in this manner is sent into commerce in iron bottles holding about 35 kilos. It contains mechanical impurities as well as other metals like lead, silver, tin, bismuth, copper, and zinc, and must be purified by first pressing through chamois or linen, and then by distilling from iron retorts. The distillation is assisted by a Torricellian vacuum. The metallic impurities may also be removed by treatment with dilute nitric acid ; this is best accomplished by running the metal into the acid in the form of a fine spray, as when it is forced through a piece of porous wood.

Properties.—At ordinary temperatures mercury is a liquid,

silver-white, lustrous metal. In very thin layers it transmits a violet-blue light. When cooled to —39.38° it forms, with considerable contraction, a malleable, ductile, and crystalline solid. Its specific gravity at 15° is 13.5584, and in the solid state 14.391.

Mercury is insoluble in water and the other usual solvents. It is not dissolved by hydrochloric acid, or at ordinary temperatures by sulphuric acid, but the latter when boiled with it slowly dissolves it with evolution of sulphur dioxide. Nitric acid, when concentrated, dissolves it rapidly.

At ordinary temperatures mercury volatilizes slowly, and when heat is applied the volatilization is increased, until at 357.25° the metal boils, and is completely dissipated, yielding a colorless and very poisonous vapor. This vapor has a specific gravity of 6.928 (air = 1).

Pure mercury may be agitated with pure air or oxygen without undergoing change, but when other metals are present it becomes grayish in color, owing to the formation of a covering of oxidation products of these metals. A globule of the metal when placed on clean white paper should roll about freely and leave no streaks, as it does when foreign metals are present.

When mercury is rubbed or agitated with fat, chalk, or honey of rose and glycerin, it is reduced to a very finely-divided condition, when it is said to be "extinguished" or "deadened." In this condition it becomes an active medicinal agent for both internal and external use.

Uses.—Besides its medicinal use, mercury is employed in the metallurgy of silver and gold, and has many uses in the laboratory, especially in barometers and thermometers.

Amalgams.—The alloys of mercury with other metals are known as amalgams. This property of dissolving other metals, which is possessed by mercury, has been likened to the solvent action of water, but in the case of the metals it is much easier to demonstrate the formation of a definite compound; thus, for instance, the compounds of mercury and silver have the composition AgHg and Ag_2Hg_3. Potassium, sodium, zinc, cadmium, tin, gold, silver, etc., dissolve readily in mercury, and in the case of potassium and sodium, with considerable evolution of heat. An amalgam of 1 part of sodium in 100 parts of mercury is viscid; with 80 parts of mercury, pasty; with 30 parts, hard.

MERCURY AND THE HALOGENS.

Mercurous Chloride, Hg_2Cl_2, *Calomel*. **Hydrargyri Chloridum Mite,** U. S. P.—The mineral *horn-quicksilver*, found native in various parts of the world, has the same composition as calomel.

Preparation.—When hydrochloric acid or a soluble chloride is added to a solution of mercurous nitrate, calomel is precipitated. The same result may be attained by passing sulphur dioxide into a solution of mercuric chloride. The product thus obtained is not satisfactory for medicinal use, as it is crystalline and granular. The salt is, therefore, usually prepared by sublimation. This is accomplished by heating a mixture of 36 parts of sulphuric acid with 24 parts of mercury, until the latter is dissolved and a dry salt remains. The mercuric sulphate thus formed is rubbed with 24 parts of mercury until the globules disappear, and then with 18 parts of common salt. The mixture is then sublimed in such a manner as to rapidly condense the vapor and form a very fine amorphous product. This is in some cases accomplished by forcing a jet of steam into the condenser with the vapor of the calomel, and in other cases by a current of cold air in like manner. The reactions involved are as follows:

$$\underset{\text{Mercury.}}{Hg} + \underset{\substack{\text{Sulphuric}\\\text{Acid.}}}{2H_2SO_4} = \underset{\substack{\text{Mercuric}\\\text{Sulphate.}}}{HgSO_4} + \underset{\substack{\text{Sulphur}\\\text{Dioxide.}}}{SO_2} + \underset{\text{Water.}}{2H_2O.}$$

$$\underset{\substack{\text{Mercuric}\\\text{Sulphate.}}}{HgSO_4} + \underset{\text{Mercury.}}{Hg} = \underset{\substack{\text{Mercurous}\\\text{Sulphate.}}}{Hg_2SO_4.}$$

$$\underset{\substack{\text{Mercurous}\\\text{Sulphate.}}}{Hg_2SO_4} + \underset{\substack{\text{Sodium}\\\text{Chloride.}}}{2NaCl} = \underset{\substack{\text{Mercurous}\\\text{Chloride.}}}{Hg_2Cl_2} + \underset{\substack{\text{Sodium}\\\text{Sulphate.}}}{Na_2SO_4.}$$

The same result may be obtained by using mercuric chloride instead of the sulphate, rubbing it with an equivalent quantity of mercury and subliming.

In both cases the product is washed well with warm water to remove mercuric chloride, since the latter is soluble in that liquid. The washing is known to be complete when ammonia causes no further turbidity with the wash-water.

Properties.—Calomel is "a white, impalpable powder, becoming yellowish-white on being triturated with strong pressure, and showing only small, isolated crystals under a magnifying power of one hundred diameters. It is odorless and tasteless, and permanent in the air." It is "insoluble in water, alcohol, or ether, and also cold dilute acids."

On the application of heat calomel is volatilized without melting. One of its most characteristic reactions is that of blackening on the addition of lime water or solution of ammonia. When concentrated hydrochloric acid is boiled with calomel, the latter is converted into mercuric chloride and mercury. Hot nitric acid

converts it into mercuric chloride and nitrate, and hot sulphuric acid also decomposes it, with evolution of sulphur dioxide and formation of mercuric chloride and sulphate.

Uses.—The chief use of calomel is in medicine.

Mercuric Chloride, $HgCl_2$, *Corrosive Sublimate.* **Hydrargyri Chloridum Corrosivum,** U. S. P.—This salt was described by Geber in the eighth century. It may be prepared in a small way by dissolving with the aid of heat 10 parts of mercuric oxide in 14 parts of 25-per-cent. hydrochloric acid, previously diluted with 28 parts of water :

$$HgO + 2HCl = HgCl_2 + H_2O.$$

The method usually employed on a large scale consists in heating 4 parts of mercury and 5 parts of sulphuric acid, with formation of mercuric sulphate :

$$Hg + 2H_2SO_4 = HgSO_4 + SO_2 + 2H_2O.$$

The dried mercuric sulphate is intimately mixed with half its weight of common salt and a little manganese dioxide to prevent formation of mercurous salts.

The dry mixture is placed in glass vessels ; these are half buried in sand and heated until the mercuric chloride is sublimed into the upper half ; the vessels are then broken, and the salt renewed. The reaction which takes place in the sublimation is as follows :

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4.$$

Properties. — Sublimed corrosive sublimate forms white, opaque, or translucent, crystalline masses, odorless, and having a sharp, metallic taste. It is permanent in the air. When rubbed in a mortar it yields a pure white powder ; calomel becomes yellow when so treated.

Corrosive sublimate is soluble in 16 parts of water at 15°, and in 2 parts of boiling water ; in 3 parts of cold and in 1.2 parts of boiling alcohol ; it is also dissolved by 4 parts of ether, and by 14 parts of glycerin.

On the application of heat the salt fuses at 265° to a colorless liquid, which at about 300° volatilizes in dense white vapors, leaving no residue. "The aqueous solution reddens litmus paper, but becomes neutral on the addition of sodium chloride." The solution in water slowly decomposes when exposed to the light, as follows :

$$2HgCl_2 + H_2O = Hg_2Cl_2 + 2HCl + O.$$

The hot acids dissolve mercuric chloride without decomposing it; this is best illustrated by the salt's subliming unchanged from its solution in concentrated sulphuric acid.

Mercuric chloride forms a number of basic chlorides; for instance, when the aqueous solution is boiled with mercuric oxide and the solution is cooled to 60°, a number of basic chlorides separate, and the clear solution poured off from these yields, on further cooling, a compound having the composition $2HgCl_2.3HgO$. When equal volumes of cold, saturated solutions of corrosive sublimate and acid potassium carbonate are mixed a compound having the composition $HgCl_2.3HgO$ separates in golden-yellow scales.

Mercuric chloride forms a large number of double chlorides with the alkali metals; these double chlorides are more soluble than the mercuric salt. When a watery solution containing equal weights of mercuric chloride and ammonium chloride is evaporated a residue is obtained, which was formerly known as *sal alembroth*, and has the composition $2NH_4Cl,HgCl_2.H_2O$. This is a powerful antiseptic, not so irritating as the mercuric salt alone.

Uses.—Mercuric chloride is a valuable agent from which to prepare the other salts of mercury. It also has extended use in medicine, especially as an antiseptic. Internally it acts as a powerful poison, except in very small doses. The best antidote is raw white of egg.

Mercurous Bromide, Hg_2Br_2, may be prepared by adding hydrobromic acid or sodium bromide to solution of mercurous nitrate; in this form it bears a close resemblance to calomel.

Mercuric Bromide, $HgBr_2$, is obtained by treating mercury under water with an excess of bromine; it crystallizes from water in glistening scales, and from alcohol in rhombic needles. It is not so soluble in water as the chloride, but is easily soluble in alcohol and in ether.

Mercurous Iodide, Hg_2I_2. **Hydrargyri Iodidum Flavum, U. S. P.**—This form of mercurous iodide has replaced the green variety which was official in the earlier Pharmacopœias, and which was prepared by rubbing in a mortar 40 parts of mercury with 2 to 3 parts of alcohol and 25.5 parts of iodine added in small portions at a time. The present official process which yields the yellow iodide consists in precipitating a solution of mercurous nitrate with one of potassium iodide:

$$Hg_2(NO_3)_2 + 2KI = Hg_2I_2 + 2KNO_3.$$

The precipitate is directed to be washed with alcohol to remove the last traces of mercuric salt, and to be kept in dark amber-colored vials, with the least possible exposure to light.

Properties.—The official salt is "a bright yellow, amorphous powder, odorless and tasteless. By exposure to light it becomes darker, in proportion as it undergoes decomposition into metallic mercury and mercuric iodide." The green mercurous iodide owes its color to the admixture with it of metallic mercury and, perhaps, some mercuric iodide.

Mercurous iodide is nearly insoluble in water, and entirely insoluble in alcohol or ether.

On the careful application of heat to 290° the salt melts to a black liquid, and then sublimes in yellow crystals. The sublimation begins as low as 120°.

Mercuric Iodide, HgI_2. **Hydrargyri Iodidum Rubrum,** U. S. P.—This salt is prepared by taking mercuric chloride, 40 parts, potassium iodide, 50 parts, each in a sufficient quantity of water, and pouring the two solutions simultaneously and in a thin stream, with active stirring, into 2000 parts of distilled water:

$$HgCl_2 + 2KI = HgI_2 + 2KCl.$$

The precipitate is well washed, dried in the dark between folds of filter paper at a temperature not exceeding 40°. The product should be kept excluded from the light. Mercuric iodide may also be prepared by rubbing in a mortar 20 parts of mercury, moistened with 2 or 3 parts of alcohol, and 25.5 parts of iodine, until a uniform product is obtained.

Properties.—Mercuric iodide is a scarlet-red, amorphous powder, without odor or taste. It is almost insoluble in water; soluble in 130 parts of alcohol at 15°, and in 15 parts of boiling alcohol. Since the salt is soluble in solution of potassium iodide and solution of mercuric chloride, it is important in its preparation that the proportion of these two salts be properly adjusted.

On the careful application of heat the salt melts at 238° to a dark-yellow liquid. It slowly sublimes without decomposition, forming yellow, rhombic crystals, which after some time become red.

Mercuric iodide readily forms double salts with the iodides; for instance, from its hot, saturated solution in potassium iodide there separates first mercuric iodide, and then by further cooling or evaporation a double salt having the composition $HgI_2, KI.1\frac{1}{2}H_2O$, in yellow prisms. This compound, under the name of *Mayer's solution*, is a useful alkaloidal reagent. A similar compound with ammonium iodide is known.

Mercurous Fluoride, Hg_2F_2, is formed by digesting calomel with silver fluoride; it forms in small, yellow crystals, soluble in water.

Mercuric Fluoride, $HgF_2.2H_2O$, forms as a white, crystalline mass when mercuric chloride is treated with an excess of hydrofluoric acid.

MERCURY AND OXYGEN.

Mercurous Oxide, Hg_2O, is obtained by precipitating mercurous nitrate with sodium or potassium hydrate. The product is an odorless and tasteless brownish-black powder, insoluble in water, and readily decomposed into mercuric oxide and mercury.

Mercuric Oxide, HgO.—The Pharmacopœia recognizes two varieties of mercuric oxide, the yellow, **Hydrargyri Oxidum Flavum**, and the red, **Hydrargyri Oxidum Rubrum.** The yellow variety is prepared by pouring a solution of 100 grammes of mercuric chloride in 1000 cubic centimeters of water into a solution of 40 grammes of sodium hydrate (90-per-cent. strength) in 1000 cubic centimeters of water:

$$HgCl_2 + 2NaOH = HgO + 2NaCl + H_2O.$$

The precipitate is well washed, and dried at a temperature below 30° without exposure to light.

The red mercuric oxide, or *red precipitate*, is prepared by dissolving 10 parts of mercury in 30 parts of nitric acid (25 per cent.), evaporating to dryness, and then heating on a sand-bath so long as yellowish vapors escape. The product obtained by the above proportions of mercury and nitric acid is a basic mercuric nitrate. On the commercial scale this basic salt is rubbed with 10 parts of mercury until the particles of the latter cease to be visible; the result is a basic mercurous nitrate which, on heating, yields mercuric oxide.

Properties.—The yellow oxide is officially described as "a light orange-yellow, amorphous, heavy, impalpable powder," while the red oxide is stated to consist of "heavy, orange-red, crystalline scales, or a crystalline powder, becoming more yellow the finer it is divided." Both varieties are odorless, with a metallic taste, and permanent in the air. The yellow oxide darkens on exposure to light. Both are almost insoluble in water, insoluble in alcohol, but readily and completely soluble in dilute hydrochloric or nitric acid, forming colorless solutions. On the application of heat both oxides become darker in color, the yellow becoming of a reddish color, and at a low red heat they are completely dissipated into oxygen and mercury.

Uses.—The oxides of mercury are used in the preparation of some of the mercurial salts, and in medicine for external use.

OXYGEN SALTS OF MERCURY.

Mercurous Chlorate, $Hg_2(ClO_3)_2$, is formed when mercurous oxide is dissolved in chloric acid, and the solution evaporated at ordinary temperatures over sulphuric acid. It is deposited in rhombic prisms which decompose at 250°, and when heated with organic matter deflagrate violently.

Mercuric Chlorate, $Hg(ClO_3)_2.H_2O$. — This salt is obtained by dissolving mercuric oxide in warm chloric acid. It crystallizes on cooling in small, rhombic pyramids.

Mercurous Sulphate, Hg_2SO_4, is prepared by heating concentrated sulphuric acid with an excess of mercury. It is a dark, crystalline powder, which melts when heated and solidifies on cooling into a crystalline mass.

Mercuric Sulphate, $HgSO_4$.—This salt is obtained as a white, crystalline mass by heating mercury with an excess of sulphuric acid. The solution in sulphuric acid is assisted by the addition of nitric acid. When gently warmed mercuric sulphate becomes yellow, then red, and at a stronger heat is decomposed into mercury, oxygen, sulphur dioxide, and mercurous sulphate. When mercuric sulphate is thrown into water it is decomposed into the basic salt.

Hydrargyri Subsulphas Flavus, U. S. P., or *Turpeth Mineral.* — This official salt is prepared by dissolving 100 grammes of mercury in a mixture of 30 cubic centimeters of sulphuric acid and 25 cubic centimeters of nitric acid, and, after drying and powdering the resulting mercuric sulphate, stirring it into 2 litres of distilled water. Basic mercuric sulphate has the composition $Hg(HgO)_2SO_4$. It is "a heavy, lemon-yellow powder, odorless, and almost tasteless; permanent in the air. Soluble in 2000 parts of water at 15°, and in 600 parts of boiling water; insoluble in alcohol; readily soluble in nitric or hydrochloric acid." On the application of heat the salt turns red, becoming yellow again on cooling. At higher temperatures it is decomposed and volatilized without leaving any residue.

Uses.—Turpeth mineral is employed in small doses as an alterative, and in larger doses as an emetic, although its use is not without some danger.

Mercurous Nitrate, $Hg_2(NO_3)_2.2H_2O$, is prepared by acting on mercury in the cold with dilute nitric acid. One part of mercury is covered in a beaker with 1.5 parts of nitric acid (25 per cent.) and set aside in a cool place for several days:

$$6Hg + 8HNO_3 + 2H_2O = 3Hg_2(NO_3)_2.2H_2O + 2NO.$$

The solution is allowed to evaporate until crystals form, when it is warmed and filtered through asbestos from the undissolved mercury. The filtrate yields the pure crystals on cooling.

Properties.—The white or colorless salt readily loses its water of crystallization. It is soluble in warm water, yielding an acid solution. In the presence of much water it is partly decomposed into a basic salt of variable composition.

Uses.—Mercurous nitrate has some use in the laboratory as a reagent, and especially for the detection of protein substances under the microscope. When used in this way it is known as *Millon's reagent*, and is prepared by dissolving 1 part of mercury in 1 part of cooled, concentrated nitric acid, and adding 2 parts of distilled water.

Mercuric Nitrate, $Hg(NO_3)_2$.—This salt is official in solution as **Liquor Hydrargyri Nitratis.** It is made by dissolving 40 grammes of red mercuric oxide in a mixture of 45 grammes of nitric acid and 15 grammes of distilled water. This solution has a specific gravity of 2.1, and contains 60 per cent. of the salt. When this solution is concentrated at ordinary temperatures over sulphuric acid it deposits deliquescent crystals, having the composition $2Hg(NO_3)_2.H_2O$. Basic salts of mercuric nitrate are readily formed.

The solution of mercuric nitrate when mixed with fat, or lard oil, forms an important official ointment, under the name of **Unguentum Hydrargyri Nitratis.**

Mercurous Phosphate, $Hg_6(PO_4)_2$, is a white, amorphous, insoluble precipitate, formed by precipitating mercurous nitrate in solution by a solution of sodium phosphate.

Mercuric Phosphate, $Hg_3(PO_4)_2$, is formed when solution of sodium phosphate is added in excess to solution of mercuric nitrate. It is a white precipitate, insoluble in water, but soluble in acids.

Mercurous Carbonate, Hg_2CO_3, exists as a light-yellow, easily decomposed powder; insoluble in water. It is prepared by precipitating mercurous nitrate with excess of potassium bicarbonate. Light must be excluded.

Mercuric Carbonate.—This compound is known only in the form of basic salts. One of these has the formula $HgCO_3,2HgO$, another $HgCO_3,3HgO$. The former is produced when potassium bicarbonate is added to solution of mercuric nitrate; the latter is formed when neutral potassium carbonate is added to solution of mercuric nitrate; both are brownish-red precipitates.

Mercuric Cyanide, $Hg(CN)_2$, is prepared by dissolving mercuric oxide in hydrocyanic acid, or by boiling 1 part of potassium ferrocyanide with 2 parts of mercuric sulphate and 8 parts of water. It is soluble in 8 parts of water, and may be crystallized from hot, aqueous solution in needles. It readily forms double salts. Formerly it was official, and had some use in medicine in place of mercuric chloride.

Mercuric Cyanate, $Hg(OCN)_2$, is obtained as a white, crystalline precipitate by adding a solution of potassium cyanate to one of mercuric chloride.

Mercuric Thiocyanate, $Hg(SCN)_2$, is prepared by precipitating a mercuric salt with potassium thiocyanate. This compound is used in the preparation of the so-called Pharaoh's serpents. The powder is made into a plastic mass with gum and water, and then formed into cones or cylinders. These, when once ignited, burn with a bluish flame and yield a bulky ash, which takes somewhat the appearance of a serpent.

MERCURY AND SULPHUR.

Mercuric Sulphide, HgS.—This compound is found in two forms, according to its method of preparation. The amorphous, black variety is produced by precipitating mercuric salts with hydrogen sulphide. The crystalline, red variety is formed by sublimation of the black compound. The red is also found in nature as *cinnabar*. It occurs in red, hexagonal prisms or in crystalline masses. The black variety was formerly known as *Ethiops mineral*.

Vermilion is a very finely-divided red sulphide prepared, usually, by subliming a mixture of 8 parts of sulphur and 42 parts of mercury.

Uses.—Mercuric sulphide was formerly used in medicine, but at the present time it is rarely employed in that way. Vermilion and cinnabar are much used in paints.

MERCURY AMMONIUM COMPOUNDS.

Mercurous Ammonium Chloride, $(NH_3)_2Hg_2Cl_2$.—When calomel is subjected to the action of dry ammonia a black compound of the above composition is formed. It is readily decomposed on heating, or by exposure to the air.

Dimercurous Ammonium Chloride, NH_2Hg_2Cl.—This compound is formed when calomel is treated with aqueous ammonia.

When mercurous nitrate is used instead of the chloride, a compound of somewhat variable composition is formed, having, presumably, the formula $NH_2Hg_2NO_3$. It was the *mercurius solubilis Hahnemanni*. It is readily decomposed on exposure to light.

Mercuric Ammonium Chloride, NH_2HgCl. **Hydrargyrum Ammoniatum**, U. S. P. *White Precipitate.*—This compound is prepared by pouring a solution of 100 grammes of mercuric chloride in 2000 cubic centimeters of warm water, into 150 cubic centimeters of ammonia water (10 per cent.), keeping the latter in excess.

$$HgCl_2 + 2NH_4OH = NH_2HgCl + NH_4Cl + 2H_2O.$$

The precipitate is collected, washed well, and dried between the folds of bibulous paper at a temperature not exceeding 30°. Light should be excluded as much as possible during the process.

Properties.—White precipitate occurs in "white, pulverulent pieces, or a white, amorphous powder, without odor, and having an earthy, afterwards styptic and metallic taste. Permanent in

the air." It is insoluble in water and in alcohol. By prolonged washing it is converted into a basic compound and becomes yellowish in color.

Warm hydrochloric, nitric, or acetic acid readily dissolves it. The salt is readily soluble in cold solution of ammonium carbonate, and in warm solution of sodium hyposulphite.

On the application of heat white precipitate is decomposed without fusion, and below redness it is completely volatilized. When heated with solution of potassium or sodium hydrate the salt turns yellow and evolves ammonia.

Uses.—White precipitate is a valuable remedy for external application.

Other compounds of mercuric ammonium chloride are known. The most important is the *Mercuric Diammonium Chloride*, $(NH_3)_2HgCl_2$, also known as *fusible white precipitate*. It may be obtained by adding 20 parts of yellow mercuric oxide to a boiling solution of 100 parts of ammonium chloride in 350 parts of water. On cooling, crystals of the above composition separate. Towards solvents this compound behaves similarly to the preceding one, but on the application of heat it readily fuses with evolution of nitrogen and ammonia.

CHAPTER VI.

ALUMINUM AND THE RARE EARTHS.

ALUMINUM.

Symbol, Al. *Atomic Weight*, 27.04. *Valence*, III or $(Al_2)^{VI}$.

History.—Alumina, the oxide of the metal, has long been known. It was formerly regarded as identical with lime: it was shown to be distinct from that substance by Marggraff in 1754. The metal was first obtained by Wöhler in 1828 by the reduction of the chloride by sodium.

Occurrence.—The most abundant sources of aluminum are the oxide and its hydrates and the silicates. The oxide is found native as corundum, of which the fine crystallized varieties constitute the gems sapphire and ruby, while the granular variety is known as emery. Of the hydrates, the monohydrate, $Al_2O_2(OH)_2$, is the mineral diaspore, the dihydrate, $Al_2O(OH)_4$, is found admixed with ferric oxide in bauxite, and the trihydrate, $Al_2(OH)_6$, as the mineral gibbsite. Of these the second is by far the most important, and is now mined both in France and in this country in Georgia and Alabama as the chief material for the preparation of alumina in the production of the metal and for the manufacture of alum. A double fluoride of aluminum and sodium is also found in Greenland as the mineral cryolite; a basic sulphate is found as alunite; and lastly numerous silicates are found in the various clays, of which kaolin or porcelain clay is the purest.

Preparation.—The first working process for the manufacture of aluminum is due to Deville, who developed and improved Wöhler's method, using the double chloride of aluminum and sodium, which he caused to react with metallic sodium, according to the reaction:

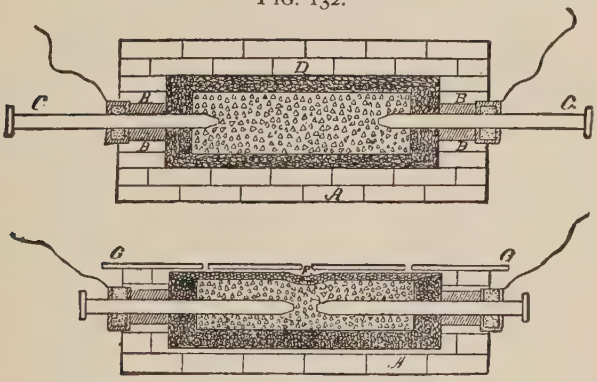
$$Al_2Cl_6.6NaCl + 6Na = Al_2 + 12NaCl.$$

This process, elaborated in 1855, remained the sole one for its manufacture for thirty years. It was an expensive method, however, in that it involved the use of the costly metal sodium and because the reaction was not capable of being made a continuous one. After the double chloride had been prepared by the action of chlorine upon a mixture of alumina, charcoal, and common salt,

it was mixed with some powdered cryolite (double fluoride of sodium and aluminum) to give fusibility to the slag, and placed in shallow trays with chips of metallic sodium. This mixture was then placed on the hearth of a reverberatory furnace previously heated to redness and the doors closed, when an energetic reaction took place. After several hours' heating the slag was run out and the melted aluminum drawn off into ingot moulds. With the advent of cheaper sodium as made by the Castner process (see p. 375) the price of aluminum as made by the Deville process was greatly reduced, but it finally was given up because of the introduction of the electrolytic methods.

In 1885 the Cowles Bros.' patent for the reduction of alumina (in the form of corundum) by carbon at the temperature of the electric arc was made public. This process is not so much adapted for the production of pure aluminum as for the formation of aluminum alloys, as aluminum bronzes (copper and aluminum). For this purpose copper is added to the mixture of broken corundum and coke, which is packed in the charcoal-lined box shown in Fig. 132, which shows the Cowles furnace in plan and

FIG. 132.

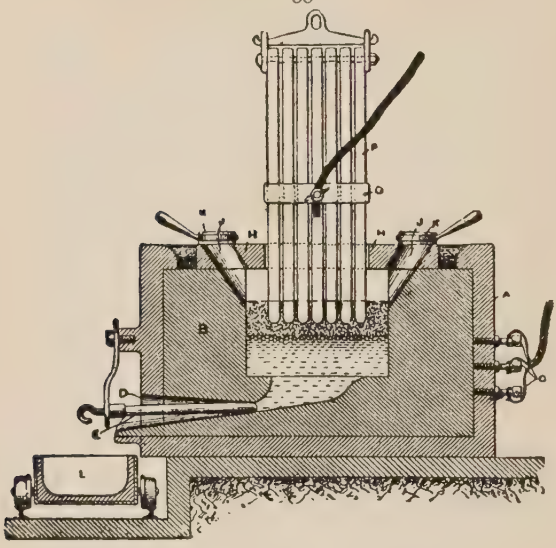


Cowles' aluminum furnace.

in longitudinal section. The heavy carbon electrodes, delivering the current from a powerful dynamo, are introduced into this mixture from the side, and can be moved so as to change the distance apart as the reduction proceeds and the conductivity of the mass changes. The alloy first obtained will contain from 15 to 30 per cent. of aluminum. This is then reduced by remelting with copper, so that alloys of from 5 to 10 per cent. of aluminum are produced, in which form they are sold. Two purely electro-

lytic processes have since been introduced,—the Heroult process in 1887 and that of Hall in 1889, and these now practically monopolize the manufacture of the pure metal. The former, as improved and carried out on a large scale at Neuhausen on the Rhine, in Switzerland, is illustrated in Fig. 133. The positive

FIG. 133.



Heroult process for aluminum.

electrode here is a bundle of carbon plates, and is suspended in the molten bath, while the negative electrode is of metal, and is introduced from below, where the metal may also be drawn off. The material to be electrolyzed is a mixture of cryolite and alumina. These works now produce daily 5000 lbs. of an aluminum of 98–99 per cent. The Hall process, as worked by the Pittsburg Reduction Co., electrolyzes a bath of a double fluoride of aluminum and sodium, to which alumina is added, from time to time, to regenerate the bath and re-form the fluoride decomposed. The metal made by this process is very pure, running over 99 per cent. The Pittsburg Reduction Co., in their new plant just finished at Niagara Falls, have a capacity of 8000 lbs. per day. The total production of aluminum in the United States in 1896 was 1,300,000 lbs., valued at $520,000, and in 1897, 4,000,000 lbs., valued at $1,542,240. A large part of this was exported to England.

Properties.—Aluminum is a bluish-white metal of high lustre, and a specific gravity of 2.56 when cast, and 2.74 when drawn into wire. It is a little softer than silver, but its ductility allows it to be drawn, punched, or spun into almost any form. It fuses at 625°, being intermediate between zinc and silver. It is practically non-tarnishable in the air, either dry or moist, and hydrogen sulphide has no action upon it. It is not acted upon by water at any temperature. Sulphuric acid does not attack it, nitric acid only slowly at a boiling temperature, but hydrochloric acid, both dilute and concentrated, dissolves it rapidly. Solutions of the alkaline hydrates also attack it rapidly, dissolving it with evolution of hydrogen and the formation of an alkaline aluminate.

Uses.—Aluminum is used in large and increasing amounts for fancy and useful articles because of the two qualities of lightness and freedom from tarnish. It is peculiarly adapted for culinary vessels, as the effect of vegetable juices and acids upon it has been shown to be less than upon tin and copper. The alloys of aluminum, however, from a commercial point of view, form its most important applications. Of these, first in importance are the alloys with copper, known as aluminum bronzes, and composed of 90–95 per cent. copper and 5–10 per cent. aluminum. These alloys are superior to brass in tensile strength, and afford superior castings. The addition of a very small amount of aluminum to other metals seems, in many cases, to allow of superior castings being made. Thus, from 0.02 to 0.04 per cent. of aluminum added to steel greatly improves it; 0.01 per cent. of aluminum added to zinc makes the molten metal thinner, and reduces the amount of oxidation that takes place in the galvanizing process; zinc with 0.05 per cent. of aluminum is also used for desilverizing bullion. The aluminum scale beams now made, which combine rigidity with lightness, contain 3 per cent. of silver and 2 per cent. of copper.

ALUMINUM AND THE HALOGENS.

Aluminum Chloride, Al_2Cl_6 or $AlCl_3$.—The determination of vapor-density shows that the chloride has the molecular weight corresponding to the former of these formulas. Hence we must assume that in this, and probably the other aluminum compounds, aluminum acts as a double atom with the valence six. The chloride is obtained by the action of chlorine at a red heat upon a mixture of alumina and carbon. Clay may be used in-

stead of alumina, but bauxite is almost universally employed, and from it alumina is prepared. Aluminum chloride is obtained in this way by sublimation in white hexagonal leaflets. It is very deliquescent, and rapidly absorbs moisture from the air. It crystallizes from concentrated hydrochloric acid solution with 6 molecules of water. The aqueous solution cannot be evaporated to dryness without decomposition into alumina and hydrochloric acid. It readily forms double chlorides with the alkaline chlorides, and the double aluminum and sodium chloride is used in the Deville process for preparing the metal. A weak solution of aluminum chloride is believed to possess disinfecting value, and is used in admixture with other chlorides for this purpose.

Aluminum Bromide, Al_2Br_6, is obtained by a method analogous to that described for the chloride, and has analogous properties.

Aluminum Iodide, Al_2I_6, is best obtained by the direct action of iodine upon aluminum. It is a white, crystalline mass, fusing at 185°, and boiling at about 400°.

Aluminum Fluoride, Al_2F_6, is formed by passing hydrogen fluoride over heated alumina, or by the reaction of aluminum sulphate and fluorspar, as now carried out on a large scale in the Grabau process for making metallic aluminum. The aluminum fluoride may then be electrolyzed, or heated with a mixture of sodium carbonate and charcoal, and the metal obtained by reduction. A double fluoride of aluminum and sodium, occurring native in Greenland as *cryolite*, is still more important in the aluminum industry. Cryolite is also the raw material for the manufacture of sodium carbonate (see p. 403) and of alum.

ALUMINUM AND OXYGEN.

Aluminum Oxide (Alumina), Al_2O_3, is found native as corundum, ruby and sapphire, and emery. Obtained artificially by igniting the hydrate, it forms a white, amorphous powder, which is insoluble in water, and fuses only at the highest temperature. Commercially it is now prepared from bauxite, either by the action of sulphuric acid or of sodium carbonate, the former process dissolving out the alumina from the impurities, and the latter making a sodium aluminate, which is soluble.

The Solvay Process Co., of Syracuse, N. Y., have recently completed a plant for making alumina from bauxite, the capacity of which is 20 tons per day.

Aluminum Hydrate, $Al_2(OH)_6$ (**Alumini Hydras**, U. S. P.), is prepared by the action of ammonium hydrate or an alkali

carbonate upon a soluble aluminum salt. The official process uses sodium carbonate and alum solutions, and then strains off the precipitate, and washes it thoroughly with hot water to remove the alkali sulphates. When freshly precipitated it is a white, gelatinous precipitate. When dried at a temperature not exceeding 40° it can be reduced to a uniformly fine white powder, which is insoluble in water or alcohol, but completely soluble in hydrochloric or sulphuric acid, and also in potassium or sodium hydrate solutions.

Gelatinous aluminum hydrate possesses the property of precipitating many dyestuffs from their solutions, forming insoluble colored compounds (*lakes*) with them. Hence the importance of aluminum compounds as mordants in dyeing. The acetate of aluminum is often used in this connection, as when the mordanted goods are steamed the acetic acid passes off, leaving the aluminum hydrate upon the fibre.

Aluminum hydrate in the presence of more electro-positive oxides can act as a weak acid and form salts called *aluminates*. Of these sodium aluminate, $Al_2(ONa)_6$, is the best known, playing an important part in the "cryolite process" for making sodium carbonate (see p. 411). Similar aluminates occur in nature as minerals, as *spinel*, or magnesium aluminate, $\begin{matrix}AlO.O\\AlO.O\end{matrix}>Mg$, *chrysoberyl*, or beryllium aluminate, and *gahnite*, or zinc aluminate.

OXYGEN SALTS OF ALUMINUM.

Aluminum Sulphate, $Al_2(SO_4)_3+16H_2O$ (**Alumini Sulphas, U. S. P.**).—This salt, with 16 molecules of water of crystallization, forms a white, crystalline powder, without odor, having a sweetish, and afterwards astringent, taste. It is readily soluble in water, but insoluble in alcohol. The salt has an acid reaction on litmus paper. A commercial sulphate with about $12H_2O$ is also manufactured on a large scale under the name of "concentrated alum," or "alum cake." A basic sulphate, $Al_2(SO_4)_3.3Al_2O_3.9H_2O$, is found native as the mineral alunite.

Aluminum sulphate unites with alkali sulphates to form a class of well characterized and crystallizable double sulphates, which are known by the general name of *Alums*. In a still wider sense, the term is applied to the whole class of double sulphates, in which we have a sesquisulphate, an alkali sulphate, and 24 molecules of water crystallizing together.

Aluminum and Potassium Sulphate (Potash Alum), $Al_2K_2(SO_4)_4 + 24H_2O$ (**Alumen**, U. S. P.), is manufactured on a large scale either from alum shale, bauxite, or cryolite. The first of these materials, which was generally used until recently, is a clay containing iron pyrites, which, on calcination, furnishes the sulphuric acid to combine with the alumina of the clay. The solution obtained by lixiviation of these heaps is concentrated and potassium chloride is added, when, on standing, the potash alum will crystallize out.

Alum forms large, colorless, octohedral crystals, having a sweetish but strongly astringent taste. On exposure to the air the crystals are liable to absorb ammonia and acquire a whitish coating. It is soluble in water, but insoluble in alcohol. When heated carefully to 200° it loses all its water of crystallization and leaves *dried alum* (**Alumen Exsiccatum**, U. S. P.), which retains all the chemical characters of the crystallized alum. The total production of alum in the United States in 1893 was between 45,000 and 55,000 tons.

Aluminum and Ammonium Sulphate (Ammonia Alum), $Al_2(NH_4)_2(SO_4)_4.24H_2O$, crystallizes in the same octohedral forms as potash alum, and is very similar in characters, but is slightly more soluble in water.

Sodium, rubidium, cæsium, silver, and thallium alums have all been prepared.

Aluminum Phosphate, $Al_2(PO_4)_2$, may be obtained by adding a solution of alum to sodium orthophosphate. The mineral *wavellite* is a basic aluminum phosphate, $2Al_2(PO_4)_2.Al_2(OH)_6.9H_2O$, occurring in rhombic crystals. Turquoise found in Persia, Silesia, and Mexico has the composition $Al_2(PO_4)_2.Al_2(OH)_6.2H_2O$.

Aluminum Silicates.—A large number of silicates found native are double silicates of aluminum and other bases. By the decomposition of these *in situ* pure aluminum silicates are often formed. Thus, one of the most abundant minerals is feldspar, a double silicate of aluminum and potassium or sodium. Its gradual decomposition with the elimination of the alkali gives rise to the large deposits of kaolin or porcelain clay, a very pure aluminum silicate. The common clays found so abundantly have resulted either from similar decomposition of aluminum silicate minerals or from their gradual comminution and deposit by aqueous agency.

Pottery and Ceramics.—The most important utilization of the clays is in the manufacture of the various grades of pottery and earthenware.

We may distinguish between the *infusible* clays, of which kaolin or

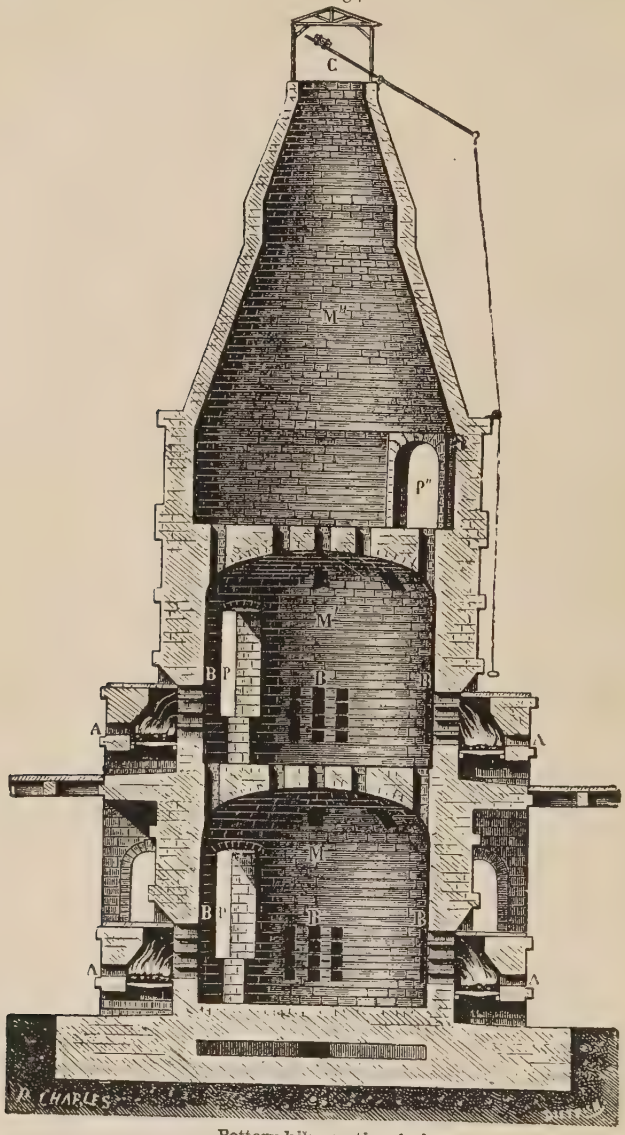
"China clay" is an example, and *fusible* clays, of which the common clays for earthenware manufacture afford examples. To these may be added the colored clays used for the brick and terra-cotta industry. The difference in chemical character of these three groups may be seen from the subjoined analyses:

	Kaolin.	Fusible Clay.	Brickmaker's Clay.
Silica	46.31 per cent.	66.38	49.44
Alumina	39.91 " "	26.08	34.26
Magnesia	0.44 " "	trace	1.94
Lime	0.43 " "	0.84	1.48
Ferrous oxide . . .	0.27 " "	1.26	7.74
Water	12.69 " "	5.14	5.14
	100.05	99.70	100.00

From kaolin, to which has been added a so-called flux, usually feldspar, is made porcelain. The materials are thoroughly admixed in a finely-ground and levigated condition with the aid of water, and after the articles are shaped on the potter's wheel or by hand they are dried and burned in the pottery kiln. This is shown in sectional view in FIG. 134. The ware is placed in vessels known as "saggers," which are arranged one above the other in columns in the compartments of the kiln as shown in FIG. 135. The baked ware is known as "porcelain biscuit," and is then to be given a glaze. This is a mixture of silicate of alumina and alkalies, and is applied in a thin cream, dried on, and then burned again in the kiln at a temperature sufficient to cause uniform fusion on the surface.

Cements.—The natural calcareous clays and artificial mixtures of similar composition are used in the manufacture of hydraulic mortars or cements. Common or Roman cements are prepared by burning natural calcareous clays or cement-rock at a temperature short of that required to cause the sintering of the mass. Portland cement, on the other hand, is made from mixtures of limestone and clay or natural cement-rock, of such composition that when burned the product will contain from 55 to 60 per cent. of lime, from 22 to 25 per cent. of silica, and some 7 per cent. of alumina. This variety is also burned until the mass is sintered together. It is then ground, allowed several months to season, and packed in barrels. These cements are essentially basic silicates of lime and alumina, and they "set" by virtue of their power of absorbing and combining with water. The production of common hydraulic cement in the United States for the year 1897 amounted to 7,721,215 bbls. of 300 lbs., and of Portland cement for the same year to 2,100,000 bbls. of 400 lbs.

FIG. 134.

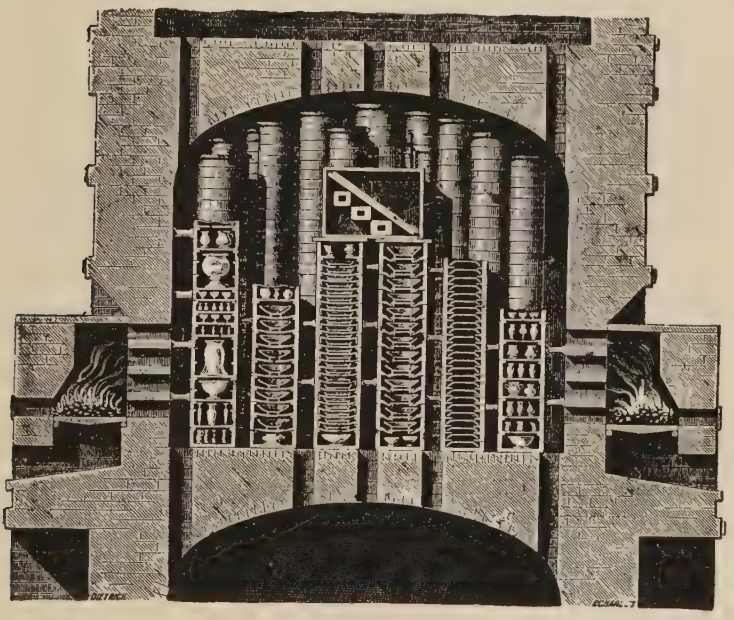


Pottery kiln, sectional view.

Ultramarine is a blue coloring matter, consisting of silica, alumina, soda, and sulphur, first found in the rare and costly mineral *lapis lazuli*, but since 1828 made artificially. A mixture of kaolin, charcoal, and sodium sulphate or carbonate is heated

to redness in closed fire-clay crucibles, and the green mass thus formed is ground to powder and then roasted in thin layers with flowers of sulphur until the required blue shade is obtained.

FIG. 135.



Interior of pottery kiln filled.

Part of the sodium in ultramarine is combined as a double silicate with alumina, and part is present as sulphide. Hence, when ultramarine is heated with hydrochloric acid, hydrogen sulphide is evolved and the blue color is destroyed.

Violet and red ultramarines are also prepared at present by conducting dry hydrochloric acid gas and air over common ultramarine at 100°–150°. The present annual production of ultramarine is about 9000 tons, of which Germany produces 6500 tons.

*Aluminum Carbonate.**—A compound of alumina with carbon dioxide, having the composition $CO_2.2Al_2O_3.8HO$, is said to be formed when solutions of aluminum salts are precipitated in the cold with solutions of alkaline carbonates. The precipitate is opaque and separates from the liquid with ease. In the dry state it is pulverulent and perfectly white. When it is treated with an acid it dissolves, giving rise to abundant liber-

* Comptes rendus, 88, 1133.

ation of carbon dioxide. This behavior distinguishes the compound from aluminum hydrate, which is obtained by mixing boiling solutions of alum and sodium carbonate. The compound is destroyed by heat. Even at 30° C. it commences to lose its carbon dioxide, and at 100° C. the disengagement is complete.

RARE EARTHS AND METALS.

In some relatively rare minerals, like cerite, gadolinite, allanite, monazite, and samarskite, occur a number of metals, the oxides of which are very analogous to alumina in chemical characters. They will be briefly enumerated, and their relationships in the list of elements pointed out.

Scandium (Sc = 43.97) is contained in euxenite and gadolinite. Its oxide, Sc_2O_3, is a white, infusible powder like magnesia. It forms a hydrate, $Sc_2(OH)_6$, and a double sulphate or alum, $Sc_2(SO_4)_3 + 3K_2SO_4$. It is interesting as having been discovered since the announcement of the periodic-system theory, and as filling a place pointed out in that system.

Yttrium (Yt = 88.9) is mostly obtained from gadolinite. It forms a potassium double sulphate, soluble in potassium sulphate solution, and thus separable from cerium, lanthanum, and didymium.

Lanthanum (La = 138.2) has been obtained by the electrolysis of its chloride as a metal resembling iron as regards color and lustre, and with a specific gravity 6.16.

Ytterbium (Yb = 172.6) is obtained from the so-called erbium earths by fractional decomposition of the mixed nitrates by heating. Its oxide, Yb_2O_3, is a white, infusible powder, of specific gravity 9.17.

These four elements form a sub-group of basic elements, attaching to aluminum in the third group of the periodic system (see p. 352).

Cerium (Ce = 139.9) occurs in cerite to the amount of 60 per cent. of the oxide. The metal has been obtained by the electrolysis of the chloride. It is very similar to lanthanum, but burns more readily. Its specific gravity is 6.72. It forms two oxides, Ce_2O_3 and CeO_2. The salts of the sesquioxide are colorless, while those obtained from the dioxide are yellow or brown.

Cerium Oxalate, $Ce_2(C_2O_4)_3.9H_2O$ (**Cerii Oxalas**, U. S. P.), "forms a white, granular powder, without odor or taste, and permanent in the air. Insoluble in water, alcohol, ether, or in solutions of potassium or sodium hydrate; soluble in diluted sulphuric or hydrochloric acid. When heated to redness it is decomposed, leaving a residue of reddish-yellow ceric oxide." Cerium nitrate has also been employed in medicine, although not official. The cerium salts are nervine tonics, and useful in cases of vomiting and dyspepsia.

The *Welsbach burner* or lamp consists of a Bunsen burner and a conoidal gauze or mantle. The Bunsen burner is attached to the usual outlet for gas. The mantle is composed of the oxides of rare metals, espe-

cially those of thorium, cerium, and zirconium, and is supported above the burner in such a way that it is heated to whiteness by the non-luminous flame of the burner. The light is emitted by the white-hot mantle.

Didymium (Di = 142) forms two oxides, Di_2O_3 and Di_2O_5. The salts of didymium by fractional crystallization can be broken up into salts of what are apparently two distinct bases, *neo-didymium* and *praseo-didymium;* the salts of the first class are rose-red and of the second yellowish-green in color.

Samarium (Sm = 149.62) was discovered in samarskite. It is very similar to didymium.

Erbium (Er = 166) forms an oxide, Er_2O_3, of reddish color, and has not certainly been obtained as yet pure.

Terbium (Tb = 159.1) occurs in large amount in samarskite. The oxide has an orange-yellow color, and otherwise resembles the oxide of erbium.

These elements all form sesquioxides, but are not as closely related to aluminum, as they seem to form higher oxides also and several series of salts.

Three heavy metals also form a sub-group belonging in the same group of the periodic system as aluminum.—viz., gallium, indium, and thallium.

Gallium (Ga = 69.9) was discovered in zinc-blende in 1875 by means of the spectroscope. It also exactly corresponded with one of the hypothetical elements indicated as possible by Mendelejeff in his periodic system. It has been obtained by the electrolysis of an ammoniacal solution of its sulphate as a white, hard metal of sp. gr. 5.9 and fusing at 30°. It forms a true alum, $Ga_2(SO_4)_3.(NH_4)_2SO_4 + 24H_2O$.

Indium (In = 113.6) was discovered in 1863 by the aid of spectrum analysis in zinc-blendes from Freiberg. It is a silvery-white, soft, and tenacious metal of sp. gr. 7.42. It fuses at 176°, and when heated burns with a blue flame. The vapor-density of the chloride corresponds to the formula $InCl_3$. It forms, however, a true alum with ammonium sulphate.

Thallium (Tl = 203.7) is rather widely distributed in nature, being found in traces with potassium in carnallite, in mineral springs, and in some pyrites and zinc-blendes. It was discovered in the chamber sludge of the sulphuric-acid works by means of the spectroscope. It is a white metal, as soft as sodium, and with a sp. gr. 11.8. It fuses at 290°, and oxidizes rapidly in moist air. It burns with a beautiful green flame, whose spectrum shows an intense green line, whence the name, from θαλλος, green. It forms two series of salts, derived from Tl_2O and Tl_2O_3.

CHAPTER VII.

THE TIN GROUP.

Tin, Germanium, and **Lead,** with **Carbon** and **Silicon,** form a group of the periodic system (see p. 346) in which the electro-negative or acid-forming character becomes weaker as we pass from carbon onward to lead. A sub-group related to these includes Titanium, Zirconium, and Thorium.

TIN (Stannum).

Symbol, Sn. *Atomic Weight,* 118.8. *Valence,* II and IV.

For many ages antecedent to any progress in the working of iron tin was known, and was employed in the production of bronze.

The Cassiterides, or "tin islands," spoken of by Herodotus are supposed to have been the British Isles, from whence, after Cæsar's conquest, tin was carried to Rome.

Occurrence.—The most important ore of tin is the mineral *cassiterite*, or tin-stone, SnO_2. When found in veins of rock it is called *vein-* or *mine-tin*, and when occurring in the beds of water-courses, *stream-tin*.

A much less frequent occurrence is as sulphide, when it is usually associated with other metals. Besides the mines of Cornwall, England, those in Malacca and Banca are important, the last named furnishing the purest product, known as *straits-tin*. Extensive mines are being developed in Australia. Tin is also found in Saxony, Bohemia, California, South Dakota, and New Hampshire.

Preparation.—When present in large quantity the ore is picked out from the rock by hand; but, ordinarily, after stamping the rock to a coarse powder, the quartz and other minerals are washed away by a stream of water.

The ore is then roasted to expel sulphur and arsenic, and afterwards lixiviated to remove copper sulphate which formed from the sulphide in the roasting process. The washed mass is mixed with powdered anthracite coal, and a little lime or fluor-spar for the purpose of forming a slag, and then reduced on the hearth of a reverberatory furnace.

The impure metal obtained is cast into ingots, which are subjected to a well-regulated heat, by which means the tin is made to melt and run off, leaving behind, as a hard mass, any iron or copper present.

The final purification is effected by agitating the molten metal. The lighter impurities rise to the surface and are skimmed off, the heavier settle to the bottom of the vessel, and from these the tin is ladled off into ingot-moulds.

Properties.—Tin is dimorphous, crystallizing in forms belonging to the isometric and the quadratic systems. It has a white, lustrous appearance, is a good conductor of heat and electricity, and, on account of the friction of its crystalline particles, it emits, when bent, a cracking sound, designated as the "cry of tin."

It is softer than zinc but harder than lead, with the exception of which its ductility is lowest of all the metals in common use, while in malleability it is surpassed by gold, silver, and copper only.

At 100° its ductility is increased, and it may be drawn into wire; at 200° it becomes brittle, and may be powdered; and at 233° it melts, being the most fusible of common metals.

The specific gravity of the metal is 7.25. Metastannic acid is produced by the action of nitric acid upon tin. Hydrochloric acid dissolves it with evolution of hydrogen and formation of chloride, while strong alkalies act in a like manner with the production of metastannates.

Tin combines directly with most of the non-metals, the character of product depending on the conditions.

Uses.—In the form of granules or foil pure metallic tin is directed by the United States Pharmacopœia to be used for the preparation of fresh stannous chloride as a reagent. The best tin hammered to the proper thinness constitutes *tin-foil*, but ordinary tin-foil consists largely of lead.

Tinned-plate is sheet-iron superficially coated with the metal, those products having the very thick layers of the coating being known as *block-tin*. Copper protected by a film of tin furnishes a valuable material for the manufacture of culinary and other utensils. Pins are brass wire coated in the same manner.

Alloys of Tin.—Tin forms with lead the useful alloys *britannia metal*, *pewter*, and *solder*, and with copper *gun-metal*, *bronze*, *bell-metal*, *speculum-metal*, and *phosphor-bronze*, the latter owing its hardness and elasticity to several per cent. of tin introduced as phosphide.

The so-called *fusible metals* contain tin as their most important constituent. *Tin-amalgam* is largely used for silvering mirrors.

TIN AND THE HALOGENS.

Stannous Chloride, $SnCl_2$.—The anhydrous salt may be obtained as a gray, fatty-looking substance by heating tin in hydrochloric acid gas, or by distilling a mixture of the powdered metal and calomel. The hydrous chloride, $SnCl_2 + 2H_2O$, which is better known, is prepared by dissolving the metal in hot hydrochloric acid. Upon evaporating the solution and cooling the salt separates as colorless prismatic needles. These are soluble in a small quantity of water, but are changed to stannous hydroxychloride by large quantities of water, unless hydrochloric acid is added. At 100° the crystals part with their water. Under the name of *tin-salts* stannous chloride finds extensive application as a mordant in dyeing and in calico-printing. It is a strong reducing agent.

Stannic Chloride, $SnCl_4$, is made by distilling tin or its amalgam with corrosive sublimate, or by conducting chlorine into a retort in which is placed tin-foil or fused tin. Thus obtained it constitutes a colorless or yellowish-fuming liquid, having a specific gravity of 2.23, and a boiling point of 120°. If to this liquid one-third of its weight of water be added, the latter combines with the stannic chloride, and a crystalline mass, known as *butter of tin*, is obtained. By dissolving the metal in a mixture of hydrochloric and nitric acids by the aid of a regulated heat, such a hydrous compound having the composition $SnCl_4 + 5H_2O$ is obtained. This last is the one best known, and is a valuable mordant for madder-red colors. Stannous and stannic bromides, iodides, and fluorides are known.

TIN AND OXYGEN.

Stannous Oxide, SnO, remains when stannous oxalate is ignited out of contact of air, or when stannous hydrate is heated.

It is a white or brown powder, soluble in acids and concentrated solutions of the alkalies.

Stannous Hydrate, $Sn(OH)_2$, is thrown down as a white precipitate upon the addition of a hydrate or carbonate to a solution of stannous chloride.

Stannic Oxide, SnO_2, occurs native as tin-stone or cassiterite. Artificially it is produced as a fine white powder by strongly heating tin or stannous oxide in free access of air. It is then known as "putty powder," and is used as a polishing agent. Ignition of stannic hydrate, obtained by precipitation, and of metastannic acid, obtained when tin is treated with nitric acid, also affords it. Stannic acid is not easily attacked by acids, even in the concentrated state.

Stannic Hydrate, Stannic Acid, H_2SnO_3, is obtained when a solution of stannic chloride is decomposed by an alkaline hydrate, or when a solution of a stannate is carefully precipitated by an acid. The stannic hydrate exhibits acid properties, reddening blue litmus paper.

Metastannic hydrate or acid, $H_{10}Sn_5O_{15}$, results when hot nitric acid acts on tin. It is distinguished from stannic acid by being altogether in-

soluble in nitric acid. Both compounds dissolve in alkalies to produce salts known as stannates and metastannates; the latter have complicated compositions.

OXYGEN SALTS OF TIN.

By far the most important compound of this class is sodium stannate, $Na_2SnO_3 + 4H_2O$. It is prepared either by fusing the stannic oxide with alkali, or the metal with alkali and sodium nitrate, or by dissolving the hydrated oxide in lye. Under the name of "preparing salts" it is extensively employed in calico-printing. The salt forms hexagonal crystals. The stannates of the alkali metals are soluble, those of the earthy and heavy metals insoluble, in water, and may be prepared by precipitation of the soluble stannates. The metastannates of the alkali metals are also used in dyeing. Stannous nitrate, stannous sulphate, stannic nitrate, and stannic sulphate are all recognized. The salts of tin possess an unpleasant metallic taste and an acid reaction.

TIN AND SULPHUR.

Stannous Sulphide, SnS, is obtained by heating together the metal and sulphur, or by precipitating a solution of stannous chloride with hydrogen sulphide.

When obtained by the first process it is a lead-gray, tough, crystalline mass; from the second method of preparation it is had as a brown precipitate, which becomes black on drying.

Stannic Sulphide, SnS_2.—This well-known compound is usually obtained by heating together tin-amalgam, sulphur, and sal-ammoniac, whereby it is obtained in gold-colored, translucent scales. It is used largely for bronzing articles of gypsum and wood, and is known as "mosaic gold."

TIN AND PHOSPHORUS.

Three phosphides of tin are known. They are respectively SnP, Sn_3P_2, and Sn_9P. The last is the only one made use of. It is a coarse, crystalline mass formed by the union of the proper quantities of the two elements, and is used for the production of phosphor-bronze.

GERMANIUM.

Symbol, Ge. *Atomic Weight*, 72.3. *Valence*, II and IV.

This extremely rare element was discovered in 1886 by Winkler in *argyrodite*, a silver ore mined at Freiberg.

Upon discovery it was found to possess the exact characteristics of the hypothetical eka-silicon, whose properties Mendelejeff, by the aid of his "Periodic Law," had predicted in 1871.

To extract the metal, the powdered mineral, which contains about 7 per cent. of the element, is fused with sodium carbonate and sulphur, the cooled mass extracted with water, and the arsenic and antimony sulphides separated by neutralizing the solution with sulphuric acid. The filtered liquid is mixed with hydrochloric acid and saturated with hydrogen sulphide, which precipitates white germanic sulphide, GeS_2. The

precipitate is washed, dried, and roasted, after which it is completely converted into germanic oxide, GeO_2, by warming with strong nitric acid. By heating this compound to redness in a current of hydrogen the metal is obtained as a dark-gray metallic powder, which is fused into a regulus by a furnace heat.

Properties.—Germanium is a white, brittle metal, with a specific gravity of 5.47. From the fused state it crystallizes in octohedra. At 900° it melts, and at higher temperatures volatilizes. Heated on charcoal it melts to a metallic globule, and, like antimony, burns with a white smoke and produces a white incrustation, both due to the formation of germanic oxide, GeO_2.

Hydrochloric acid fails to dissolve the metal, which is readily soluble in nitrohydrochloric and also in concentrated sulphuric acids to form soluble compounds. Nitric acid converts it into white germanic oxide, GeO_2, while concentrated solution of potassium hydrate is without action. Zinc slowly separates the metal from its solutions.

COMPOUNDS OF GERMANIUM.

Like most of the members of the tin group to which this metal through many of its properties is related, germanium forms two series of compounds,—viz., *germanous* and *germanic*.

The dissimilarity of its compounds to the corresponding ones of the allied metals is frequently evinced by the solubility and volatility which characterize the former.

Germanous Chloride, $GeCl_2$, is a colorless, strongly-smelling liquid, obtained by heating the powdered metal in hydrochloric acid gas. It boils at 72°.

When direct union of the metal and chlorine takes place, germanic chloride, $GeCl_4$, is produced. In appearance and odor it resembles germanous chloride, but has a boiling point of 86°.

Germanic Iodide, GeI_4, is an orange-yellow powder.

Germanous Oxide, GeO, is obtained by decomposing germanous chloride by potassium hydrate. In hydrochloric acid solution it acts as a strong reducing agent. Germanic sulphide and oxide have been previously mentioned.

LEAD (Plumbum).

Symbol, Pb. *Atomic Weight*, 206.4. *Valence*, II and IV.

History.—Lead has been known from the earliest times. It was designated *Saturn* by the alchemists, who believed that some connection existed between the metals and the planets.

Occurrence.—Lead has been found in nature uncombined, but in small quantity only, as in certain volcanic tufa. The oxides of lead are found in a few rare minerals. By far the most abundant and important ore of lead is the sulphide or *galena*, PbS ; this is very widely distributed, usually occurring with quartz, fluor-spar,

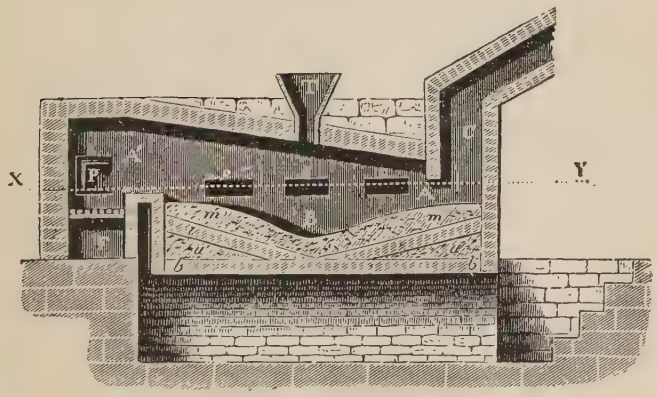
calc-spar, and heavy spar. The most important deposits in England are those of Cornwall and Cumberland. In the United States there are two localities which furnish the chief supply of lead,—the Rocky Mountain district, in which the lead is a by-product in the preparation of silver, and the Mississippi Valley district, in which galena is worked for lead alone. The ores are known respectively as argentiferous and non-argentiferous, the former furnishing by far the greater proportion of lead. *Cerussite* or native carbonate, $PbCO_3$, and *anglesite* or native sulphate, $PbSO_4$, are ores of minor importance when compared with galena.

The total production of lead in the United States during 1897 amounted to 194,530 tons, valued at $13,931,348. The total production of the world during that time amounted to something over half a million tons.

Extraction.—Lead is almost exclusively prepared from galena. In case the ore is nearly free from other metallic sulphides and silica, it is roasted in a reverberatory furnace, whereby a part of the sulphide is converted into oxide and sulphate; air is then excluded, the temperature is increased, when the following reactions take place with formation of metallic lead:

$$PbS + 2PbO = 3Pb + SO_2.$$
$$PbS + PbSO_4 = 2Pb + 2SO_2.$$

FIG. 136.

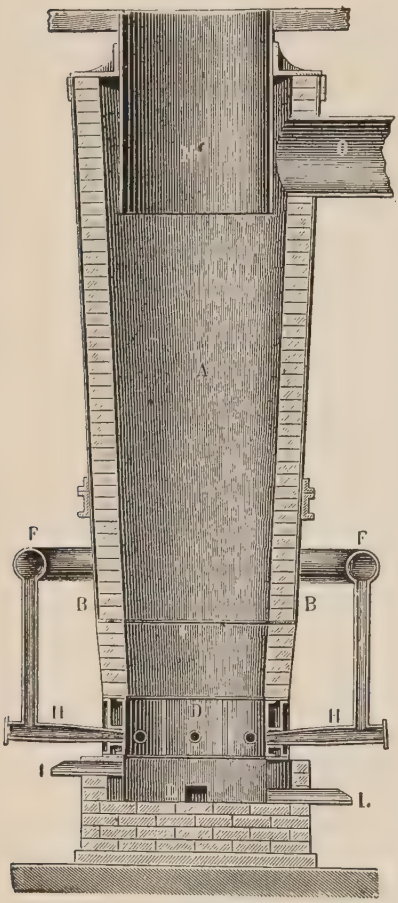


Lead furnace.

This is known as the *air reduction process*, and is conducted in a furnace as shown in Fig. 136. The furnaces are constructed to

hold 20 tons of ore, which is introduced at T, and evenly spread over the hearth, which is hollowed out at B, so as to allow the metal to collect, and from which it can be drawn out by a taphole into an iron pot. When the ore is impure, charcoal is used to assist in the reduction. Small quantities of other metals are removed by melting the lead, and subjecting it to the oxidizing action of a current of air in a reverberatory furnace. The impurities oxidize first, rise to the surface, and are removed as slag.

Fig. 137.



Lead furnace.

Iron is sometimes used as a reducing agent. This is accomplished by placing alternate layers of the ore and an iron slag in a blast-furnace (Fig. 137). In this process a portion of the lead is reduced by the metallic iron, a considerable residue, however, remaining behind in the form of sulphide, together with the sulphides of iron and other metals contained in the ore. This slag or lead regulus is then worked up according to the character of the metals of which it is composed. Sometimes copper is a constituent, in which case it may be so rich in that metal as to pay for extracting it.

When argentiferous lead ores are worked the process becomes modified according to the richness of the ore in silver, or the lead is further treated. If silver predominates, the ore is oxidized and cupelled as described under that metal. It is much oftener the case that the lead predominates, when Pattinson's process is employed. This consists in cooling the melted metal, when pure

lead first crystallizes out and is removed by perforated ladles. In this way a metal very rich in silver is obtained, which is cupelled.

Parke's process for desilvering lead is based on the fact that melted lead and zinc do not mix in all proportions. By adding, therefore, a certain proportion of zinc to the argentiferous lead, an alloy of zinc and silver is formed, which rises to the top and solidifies. It is then easily removed.

Properties.—Lead is a bluish-gray, lustrous metal; it is soft and malleable, but is not capable of being drawn into wire. It is easily cut with a knife, and when drawn over white paper leaves a gray streak. Lead melts at 327.7°, and quickly becomes covered with a layer of oxide; at a red heat it vaporizes slowly; and when heated to whiteness, distils. Melted lead crystallizes, when cooled slowly, in regular octohedrons. The specific gravity of lead is 11.37.

Pure water does not dissolve lead so long as air is excluded; when, however, air is present, lead hydrate is formed, which is slightly soluble in water. Rain water and distilled water also dissolve minute quantities of lead; hot water containing small proportions of various salts, notably chlorides and sulphates, does not dissolve the metal. With most natural waters, therefore, lead pipes may be employed. Carbonated waters should not be passed through such pipes, unless the latter are well tinned on the inner surface.

Concentrated hydrochloric or sulphuric acid attacks lead but slowly, even when warmed, but nitric acid dissolves it readily. Weak acids like acetic will dissolve it in the presence of air.

Uses.—On account of its power to resist the action of air, water, and acids, lead is employed for a great variety of purposes. Enormous quantities are used in the manufacture of lead pipe. It is also the best material for lining sulphuric acid chambers. Bullets and shot are made of lead; the latter contain one-half per cent. of arsenic in order to give them a spherical form.

Alloys of Lead.—Lead enters largely into the composition of a number of useful alloys. *Type-metal* is composed of 2 parts lead, 1 part each of antimony and tin. *Solder* consists of 1 part lead and 2 parts tin; a common variety is made of equal parts of these two metals.

LEAD AND OXYGEN.

Lead Suboxide, Pb_2O.—This compound is formed on the surface of melted lead when the temperature is not too high. It may be prepared

by heating lead oxalate in an atmosphere free from oxygen and at a temperature below 300°. It is a black, velvety powder, which, if heated without access of air, decomposes into the metal and monoxide.

Lead Monoxide, PbO. **Plumbi Oxidum**, U. S. P. *Litharge.*—A rare mineral found near Vera Cruz is composed of this substance. There are two varieties of lead oxide in commerce,—namely, *massicot*, which is yellow in color and prepared by carefully heating lead carbonate or nitrate to low redness, and *litharge*, which has been prepared at a much higher temperature, and is a by-product in the desilverization of lead ores. Litharge is obtained at a temperature sufficiently high to fuse it, and in solidifying it forms shining, scaly masses, which are sometimes of a yellowish color, but oftener inclining to red.

Properties.—The official oxide is "a heavy, yellowish, or reddish-yellow powder, or minute scales, without odor or taste. On exposure to the air it slowly absorbs moisture and carbon dioxide." It is almost insoluble in water, but when left in contact with it imparts to it an alkaline reaction. It is insoluble in alcohol, but soluble in acetic and dilute nitric acids, and in solutions of sodium and potassium hydrates.

On the application of heat lead oxide assumes a brownish-red color, and at a red heat it fuses. When heated before the blowpipe on charcoal it yields metallic lead.

Uses.—Litharge is extensively used in the manufacture of flint glass, and is a constituent of the glaze used for earthenware. It is also useful as a starting-point for a number of other lead compounds.

Lead Sesquioxide,, Pb_2O_3, is formed as a reddish-yellow powder when cold solution of lead hydrate in sodium hydrate is mixed with a solution of sodium hypochlorite, or when a solution of red lead in acetic acid is precipitated by very dilute ammonia. It is decomposed by acids into the monoxide and dioxide, and is therefore considered to be a mixture of these two.

Red Lead or *Minium*, Pb_3O_4.—When litharge is carefully heated this oxide is formed. The commercial product is of variable composition. It is used as a pigment and in the preparation of the finer kinds of flint glass.

Lead Dioxide or *Peroxide*, PbO_2.—This is also known as *puce-colored lead oxide.* It is obtained by boiling lead acetate solution with solution of bleaching powder, or in the dry way by heating 4 parts of litharge with 8 parts of potassium nitrate and 1 part of potassium chlorate. It is also readily obtained by heating red lead with nitric acid.

Lead peroxide is a dark-brown, amorphous powder, which is readily decomposed by heat into lead monoxide and oxygen. It occurs native

in black, hexagonal prisms as *plattnerite*. Lead peroxide has a strong oxidizing action on many compounds, especially those of an organic character.

Lead Hydrate, $Pb(OH)_2,PbO$.—This is more properly called oxyhydrate. It is obtained as a white precipitate when solution of lead acetate or nitrate is treated with so much solution of sodium or potassium hydrate as is necessary to produce an alkaline reaction. It is insoluble in water, but easily soluble in excess of sodium or potassium hydrate, forming the compounds $Pb(ONa)_2$ and $Pb(OK)_2$. When solutions of these are boiled the yellow or red lead oxide separates according to the concentration of the solution.

LEAD AND THE HALOGENS.

Lead Chloride, $PbCl_2$, is found to some extent in nature as the mineral *cotunite*. It is most readily prepared by adding sodium chloride to a solution of lead nitrate or acetate, although it may be obtained by dissolving lead in hot aqua regia.

Lead chloride occurs in white, pearly crystals, soluble in 135 parts of cold water and in about 30 parts of that liquid at the boiling temperature. At 498° the crystals melt, and on cooling form a horny mass.

A number of oxychlorides are known which are employed as pigments; *Cassel's yellow* is one of these; it is prepared by heating together lead oxide and sal-ammoniac. The oxychloride, $PbO,PbCl_2$, is found in nature as the mineral *matlockite*.

Lead Bromide, $PbBr_2$, is obtained by treating a soluble lead salt with solution of potassium bromide. In many respects it resembles the chloride.

Lead Iodide, PbI_2. **Plumbi Iodidum, U. S. P.**

Preparation.—1 part of lead nitrate in 20 parts of water is poured, with constant stirring, into 1 part of potassium iodide in 10 parts of water:

$$Pb(NO_3)_2 + 2KI = PbI_2 + 2KNO_3.$$

The resulting precipitate is collected on a filter, washed well with cold water, and carefully dried. Instead of the lead nitrate, one may use 9 parts of lead acetate in 90 parts of water acidified with a little acetic acid, and 8 parts of potassium iodide in 80 of water.

Properties.—Lead iodide is a heavy, lemon-yellow powder, without odor or taste; soluble in about 2000 parts of water at 15° and in 200 parts of boiling water, "separating from the latter solution in brilliant, golden-yellow spangles or crystalline laminæ. Very slightly soluble in alcohol, but soluble, without color, in solutions of the fixed alkalies, in concentrated solutions of the acetates of the alkalies, of potassium iodide, and of sodium hypo-

sulphite, and in a hot solution of ammonium chloride. When moderately heated, the salt fuses to a thick, reddish-brown liquid, which congeals, on cooling, to a yellow, crystalline mass. At a higher temperature it is decomposed, with the evolution of vapors of iodine, leaving a lemon-yellow residue of lead oxyiodide."

Uses.—The principal use of lead iodide is in medicine, where it is employed externally in the form of an ointment.

Lead Fluoride, PbF_2, is precipitated as a white insoluble powder when hydrofluoric acid is added to a soluble salt of lead.

OXYGEN SALTS OF LEAD.

Lead Sulphate, $PbSO_4$, is found in nature as *lead vitriol* or *anglesite*, in transparent rhombic crystals. These crystals are isomorphous with those of strontium and barium sulphate.

Lead sulphate is prepared by precipitating lead nitrate or acetate with sodium sulphate. It is only slightly soluble in water and in dilute acids, but somewhat more soluble in concentrated sulphuric acid. Hot concentrated nitric acid dissolves it, and it is readily soluble in solutions of sodium thiosulphate or ammonium acetate.

Lead sulphate is a by-product in the manufacture of aluminum acetate in calico print-works and dyeing establishments. It is used to mix with other lead compounds in the manufacture of paint and in the manufacture of lead chromate.

Lead Nitrate, $Pb(NO_3)_2$. **Plumbi Nitras, U. S. P.**

Preparation.—This salt is prepared by adding, in small portions at a time, 10 parts of lead oxide to 23 parts of nitric acid (25 per cent.), previously mixed with an equal weight of water and warmed :

$$PbO + 2HNO_3 = Pb(NO_3)_2 + H_2O.$$

The solution is filtered, and, after the addition of a few drops of nitric acid, is set aside to crystallize.

Properties.—Lead nitrate crystallizes in large, anhydrous, regular, mostly octohedral crystals, isomorphous with the nitrates of barium and strontium. When these crystals separate from hot solutions they are white and opaque, but if formed by the spontaneous evaporation of cold solutions they are transparent. The salt is soluble in 2 parts of water and in 0.75 part of boiling water ; almost insoluble in alcohol. On the application of heat nitrous fumes are evolved and a residue of lead oxide remains.

Uses.—Lead nitrate is used extensively in the manufacture of mordants for use in dyeing and calico-printing, and in the manufacture of lead chromate.

Lead Nitrite, $Pb(NO_2)_2$, is obtained by decomposing silver nitrite with lead chloride. The solution is concentrated in a vacuum, when yellow, prismatic crystals separate, which are readily soluble in water.

Lead Phosphate, $Pb_3(PO_4)_2$, forms as a white precipitate when solutions of lead acetate and sodium phosphate are mixed. When phosphoric acid is added to a boiling lead nitrate solution, lustrous, white crystals having the composition $PbHPO_4$ separate.

Lead Borates.—A number of these salts appear to exist, one of which is obtained by precipitating a soluble lead salt with solution of borax. It appears to have the composition $Pb_2B_6O_{11}.4H_2O$.

Lead Silicates.—These compounds are formed in the manufacture of some kinds of glass. When equal weights of lead oxide and silica are fused together a yellow glass is formed.

Lead Carbonate, $PbCO_3$.—The normal lead carbonate is found in nature as the mineral *cerussite*, or it may be artificially prepared by precipitating a solution of lead acetate with one of ammonium carbonate. This compound is not much used.

Basic Lead Carbonate, $(PbCO_3)_2Pb(OH)_2$. **Plumbi Carbonas**, U. S. P. *White Lead.*—This compound was known to the ancients.

Preparation.—White lead is manufactured on a large scale by the following processes :

1. *The Dutch Process* is the oldest, and is employed in Holland, Belgium, and some parts of Germany. It consists in placing coils or buckles of lead in earthenware pots, in the bottom of which is a small quantity of vinegar. The lead is placed on projections in the pots so as not to come in direct contact with the liquid; the walls of the pots are perforated just above the vinegar, so as to allow a free circulation of air and gas. A number of the pots are placed together as shown in Fig. 138, and

FIG. 138.

Dutch process for making white lead.

after covering each with a wooden plate they are surrounded with horse manure or spent tan-bark. The fermentation of the manure or tan causes the requisite elevation of temperature to vaporize some of the acetic acid

of the vinegar, which acts on the lead with the formation of basic lead acetate. This is slowly converted into carbonate by the carbon dioxide which results from the fermentation. After some weeks the lead will be found wholly converted into basic carbonate.

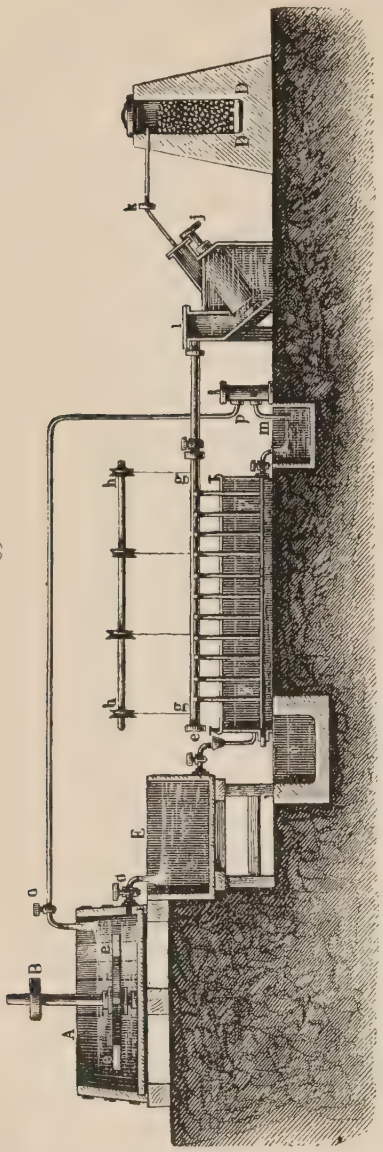


FIG. 139.—The Clichy white-lead process.

2. In the *English Method* sheet-lead is melted on the hearth of a reverberatory furnace so as to convert it into oxide, and this, in turn, is intimately mixed with a small quantity of solution of lead acetate. The resulting mass is placed in a series of closed troughs communicating with one another, and so arranged as to admit the passage of a current of carbon dioxide. This gas is obtained by the combustion of coke in a furnace provided with a blast to give impulse to the gas.

3. The *German* or *Austrian Method* involves the action of acetic acid and carbon dioxide on sheets of lead as in the Dutch process, but a large number of the lead coils are placed in a room with vinegar and tan on the floor. The tan is caused to ferment and furnish the necessary carbon dioxide.

4. The *French Method* consists in dissolving an excess of lead or lead oxide in acetic acid, so as to form basic lead acetate, and then passing carbon dioxide into this solution, by which means two molecules of lead oxide are converted into basic carbonate, while neutral acetate of lead remains. This is again converted into basic acetate, which is, in turn, decomposed by more carbon dioxide.

The principle involved in this method was first explained by Thénard, but it is generally known as the *Clichy Process*, because of the works

located at Clichy, near Paris. Fig. 139 shows a plan of these works. In the tub A, the litharge is dissolved in acetic acid, the solution being aided by means of the stirrer *e e*. The solution of basic lead acetate is run into the vessel E, where the impurities subside, and the clear solution is then run into the decomposing vessel F F, which is supplied with several hundred tubes for the admission of the carbon dioxide. In from 12 to 16 hours the conversion is complete. The neutral lead acetate is run into the tank *m* and returned to A, while the semi-liquid basic lead carbonate is drawn into the tank O. The carbon dioxide is generated in D and purified in the vessel *j*.

Many more processes have been patented and worked in a small way in the production of white lead, but it is probable that in this country, as well as in most foreign countries, the Dutch method is given the preference.

The product in all the foregoing processes is finely ground with water, well washed to remove lead acetate, and finally dried.

Some white lead is made from lead sulphate by heating together this salt and solution of sodium hydrate, whereby a basic lead sulphate is formed, and this, by boiling with sodium carbonate solution, is converted into basic lead carbonate and sodium sulphate.

Properties.—Basic lead carbonate is a heavy, white, amorphous powder. It is without odor or taste, and is permanent in the air. Water and the other ordinary solvents do not dissolve it, but acetic acid and dilute nitric acid readily dissolve it with effervescence. When heated to 200° it turns yellow without charring, and gives off its carbon dioxide, leaving a residue of oxide.

Uses.—White lead is frequently mixed with gypsum, and with barium sulphate or heavy spar. *Hamburg white* is a mixture of 1 part white lead and 2 parts barium sulphate. *Dutch white* contains 3 parts of the barium sulphate to 1 part of white lead. The amount of barium or calcium salt is readily determined by treating the powder with warm acetic or dilute nitric acid, which will dissolve only the lead salt. Lead sulphate is sometimes used as an adulterant. The chief objection to it is its deficient covering power when made into paint.

Paint is chiefly made by grinding white lead with oil, and then thinning with linseed oil or oil of turpentine, according to the use to which it is to be applied.

LEAD AND SULPHUR.

Lead Sulphide, PbS, is very widely distributed in nature as a strongly lustrous, bluish-gray mineral. It may be artificially prepared by passing hydrogen sulphide into a solution of lead acetate. It is a black, insoluble powder, which is scarcely dissolved by hydrochloric acid, but converted

by hot concentrated nitric acid into lead sulphate. At a red heat it melts, and it may be sublimed in a current of carbon dioxide or hydrogen. Lead sulphide is used in the glazing of certain kinds of pottery-ware.

TITANIUM.

Symbol, Ti. *Atomic Weight,* 48. *Valence,* IV.

Occurrence.—Titanium occurs as oxide, TiO_2, under the names of *rutile*, *anatase*, and *brookite*, and in titanates such as $CaTiO_3$ and $FeTiO_3$.

Preparation and Properties.—The metal is a gray, metallic powder, and has been obtained by heating the double fluoride, K_2TiF_6, with potassium. It burns when heated in the air, and is dissolved by dilute hydrochloric and sulphuric acid with evolution of hydrogen.

COMPOUNDS OF TITANIUM.

Titanium Chloride, $TiCl_4$, and *Titanium Fluoride*, TiF_4, are known. The latter forms compounds like K_2TiF_6, analogous to the silico-fluoride of potassium, K_2SiF_6.

Titanic Acid, H_4TiO_4, is obtained as a white, amorphous powder on adding ammonium hydrate to the hydrochloric acid solution of the titanates. It readily loses 1 molecule of H_2O, and becomes $TiO(OH)_2$, analogous to $CO(OH)_2$.

Titanium Dioxide, TiO_2, is abundantly found in nature. It is almost insoluble in the acids, being dissolved only by hydrofluoric acid. It forms titanates on fusion with the alkalies.

ZIRCONIUM.

Symbol, Zr. *Atomic Weight,* 90.4. *Valence,* IV.

Zirconium is relatively rare, being generally found as the silicate, $ZrSiO_4$, called *Zircon*. The metal can be obtained as an amorphous black powder or in crystalline metallic leaflets.

Zirconic Acid or *Hydrate*, $Zr(OH)_4$, is precipitated from acid solutions as a white, voluminous precipitate, which, on ignition, leaves

Zirconium Dioxide, ZrO_2.—Both this oxide and the hydrate dissolve when warmed with sulphuric acid, forming $Zr(SO_4)_2$, which may be crystallized from water.

THORIUM.

Symbol, Th. *Atomic Weight,* 231.9. *Valence,* IV.

Thorium occurs only in rare silicates, such as *thorite*. The free metal has been obtained as a light-gray, crystalline powder which burns in the air to the dioxide.

Thorium Hydrate, $Th(OH)_4$, and *Thorium Dioxide*, ThO_2, do not form salts with the alkalies, but dissolve in sulphuric acid to form $Th(SO_4)_2$.

CHAPTER VIII.

THE ARSENIC GROUP.

ARSENIC.

Symbol, As. *Atomic Weight*, 74.9. *Valence*, III and V.

History.—Arsenic in the form of its two sulphides, *realgar* and *orpiment*, was known to the ancients. Schroeder, in 1694, appears to have been the first to separate the metal.

Occurrence.—Arsenic is widely distributed in nature; in the free state it is occasionally found in distinct crystals, but oftener in kidney-shaped masses, which readily split into laminæ. Native arsenic has been found in Saxony, Bohemia, and various other parts of Europe, at San Augustin, in Mexico, and at Haverhill, New Hampshire, in the United States. In the combined state arsenic is more abundantly distributed; as white arsenic, As_2O_3, as orpiment, As_2S_3, and as realgar, As_2S_2, it is well known; but its most important occurrence is in the form of arsenical iron, $FeAs_2$, and arsenical pyrites or mispickel, $FeAs_2$,-FeS_2. Certain cobalt and nickel ores also contain considerable quantities of arsenic. Small quantities of arsenic are found in many mineral waters and in sea water.

Preparation.—Metallic arsenic is prepared by subliming the native mineral or by reducing arsenous oxide with charcoal:

$$As_2O_3 + 3C = 2As + 3CO.$$

Probably the largest quantity is prepared by subliming arsenical pyrites:

$$FeAs_2,FeS_2 = 2As + 2FeS.$$

Properties.—Arsenic is a steel-gray, lustrous metal, which occurs in several allotropic modifications. When heated quickly in a tube through which hydrogen is passing, there separate nearest the heated portion of the tube distinct crystals; next to these the metal deposits in a black, amorphous mass, and still farther away a gray, amorphous powder is condensed. The crystalline variety has a specific gravity of 5.727, while that of the two amorphous varieties is 4.710. The amorphous varieties become crystalline when heated to 360°. In dry air arsenic undergoes no change, but in moist air it becomes oxidized in part to arsenous

oxide. When heated in air the metal burns to arsenous oxide, but when heated without access of air, it vaporizes without previously melting.

Uses.—Metallic arsenic is chiefly used in the manufacture of shot to give a globular form to the grains. Cobalt glance, a compound of arsenic and cobalt, has considerable use as a fly-poison under the name of *fly-stone*.

ARSENIC AND HYDROGEN.

Hydrogen Arsenide or *Arsine*, AsH_3.—In order to prepare arsine in a pure state, an alloy of zinc and arsenic, As_2Zn_3, is treated with dilute sulphuric acid:

$$As_2Zn_3 + 3H_2SO_4 = 2AsH_3 + 3ZnSO_4.$$

This reaction should be carried out with the greatest care, as the gas is extremely poisonous. Gehlen lost his life by it in 1815. Arsine is a colorless, disagreeably-smelling gas, which when once ignited burns in the air with the formation of arsenous oxide and water. If the flame be cooled by the introduction of a cold, porcelain surface, black, shining, metallic arsenic is deposited. *Marsh's test* (see Qualitative Test, Part V.) depends on this property. When arsine is passed into a solution of silver nitrate, metallic silver is precipitated as follows:

$$6AgNO_3 + AsH_3 + 3H_2O = 3Ag_2 + 6HNO_3 + H_3AsO_3.$$

If the gas be passed through a tube and flame be applied at one point so as to bring the tube to low redness, the gas is decomposed and a brilliant layer of metallic arsenic is deposited; this also serves as a method of detecting the element.

Solid Hydrogen Arsenide, As_2H_2, is formed as a brown, silky mass when sodium arsenide, $AsNa_3$, is decomposed by water.

ARSENIC AND THE HALOGENS.

Arsenic Trichloride, $AsCl_3$, may be prepared by passing dry chlorine over powdered arsenic; but it is more easily obtained by heating to the boiling point of water 40 parts of arsenous oxide with 100 parts of concentrated sulphuric acid in an apparatus connected with a well-cooled receiver; small pieces of fused sodium chloride are then thrown in, when the following reaction takes place:

$$6HCl + As_2O_3 = 2AsCl_3 + 3H_2O.$$

The water which is liberated is retained by the sulphuric acid.

Properties.—Arsenic trichloride is a colorless, oily liquid, having a specific gravity of 2.205. It boils at 134°, forming a colorless vapor. When brought in contact with a large quantity of water, the oxychloride, $As(OH)_2Cl$, separates.

Arsenic Tribromide, $AsBr_3$, forms colorless, deliquescent crystals, which melt at 20° to 25°, and the resulting liquid boils when heated to 220°.

Arsenic Tri-iodide, AsI_3. **Arseni Iodidum**, U. S. P.—This official compound is prepared, according to the Pharmacopœia of 1870, by rubbing intimately together 1 part of metallic arsenic with 5 parts of iodine and subliming the product. It is more readily made by taking a hot saturated solution of arsenous oxide in hydrochloric acid, and adding to it a concentrated aqueous solution of potassium iodide, when the tri-iodide separates in crystals.

Properties.—Arsenic tri-iodide is usually seen in "glossy, orange-red crystalline masses, or shining, orange-red crystalline scales, having an iodine-like odor and taste, and gradually losing iodine on exposure to air and light." It is soluble in 7 parts of water at 15°, and in about 30 parts of alcohol; soluble in ether and in carbon disulphide. Boiling water gradually decomposes it. "The aqueous solution has a yellow color, is neutral to litmus paper, and, on standing, is gradually decomposed into arsenous and hydriodic acids." It is one of the active ingredients of *Donovan's Solution*, **Liquor Arseni et Hydrargyri Iodidi**, U. S. P.

Arsenic Di-iodide, As_2I_4, is formed as a cherry-red crystalline mass by heating in a sealed tube, to 230°, 1 part of arsenic with 2 parts iodine.

Arsenic Penta-iodide, AsI_5, is prepared in the same manner as the foregoing, by using 1 part of arsenic to 8.5 parts of iodine.

Arsenic Trifluoride, AsF_3, is prepared by distilling 4 parts of arsenic trioxide with 5 parts of fluorspar and 10 parts of concentrated sulphuric acid. It is a colorless liquid, boiling at 63°.

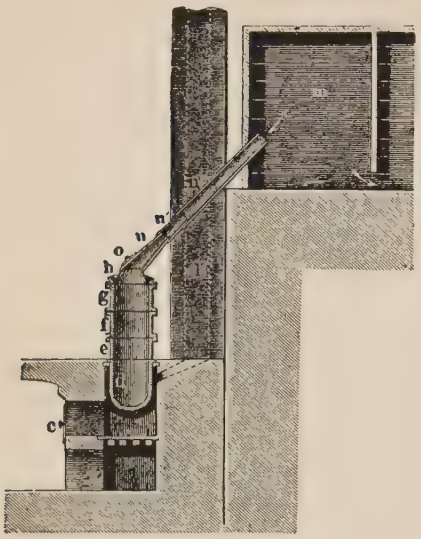
ARSENOUS OXIDE AND ARSENITES.

Arsenous Oxide, As_2O_3. **Acidum Arsenosum**, U. S. P. *Arsenic Trioxide*, *White Arsenic*.—This compound was known in the eighth century, and was prepared by roasting the sulphide. It occurs in nature in two rare minerals.

Preparation.—Arsenous oxide is obtained as a by-product in various metallurgical operations. Cobalt and nickel ores are especially rich in arsenic, and the fumes from the roasting of these ores are passed through a series of chambers, in which the arsenous oxide is condensed in an impure condition. In Silesia arsenical pyrites are roasted especially for the arsenic. In England large quantities are obtained in the roasting of tin ores. When resulting as a by-product, arsenous oxide is usually in fine powder and quite impure, and requires to be sublimed. This is accomplished by the apparatus shown in Fig. 140. *d* is an iron

vessel in which the oxide is heated; on this are placed a number of iron cylinders, *e*, *f*, *g*, *h*, which are connected by the tubes *o*, *n*, *n'*, with the chamber *m*. In the cylinders the oxide condenses as an amorphous, opaque, glassy solid, while in the tubes and chambers it is deposited as a crystalline powder.

FIG. 140.



Sublimation of arsenous oxide.

Properties.—Arsenous oxide occurs in two modifications, amorphous and crystalline; the former is transparent and colorless like glass, while the latter is opaque or white, resembling porcelain. The glassy variety gradually changes to the opaque form. Both are odorless and tasteless.

"In cold water both varieties dissolve very slowly, the glassy variety requiring about 30, the porcelain-like about 80 parts of water at 15°. Both are slowly and completely soluble in 15 parts of boiling water. In alcohol, Arsenous Acid is but sparingly soluble, but it is soluble in about 5 parts of glycerin. Oil of turpentine dissolves only the glassy variety. Both varieties are freely soluble in hydrochloric acid, and in solutions of alkali hydrates and carbonates."

On the application of heat the oxide volatilizes completely at 218° without melting, and if its vapor be passed over charcoal in a tube, it is reduced to the metal and deposited on the glass as a mirror.

Arsenous Acid, H_3AsO_3, is not known in the free state, but when arsenous oxide is dissolved in water it imparts to the latter a feebly acid reaction. The following salts are the most important:

Potassium Arsenite. **Liquor Potassii Arsenitis,** U. S. P.—The official process consists in boiling 10 grammes of arsenous oxide with 20 grammes of potassium bicarbonate and 100 c.c. of water until a clear solution is effected, and then diluting with

sufficient water and 30 c.c. of compound tincture of lavender to make 1000 c.c. The product is used in medicine under the name of *Fowler's solution*. Only the alkali arsenites are soluble in water.

Cupric Arsenite, $CuHAsO_3$, *Scheele's Green*, is an insoluble green powder used as a pigment.

Paris Green is a cupric aceto-arsenite made by boiling together solutions of copper acetate and arsenous oxide. It has the formula $Cu(C_2H_3O_2)_2,3Cu(AsO_2)_2$.

Arsenous oxide is one of the compounds most frequently employed as a poison. Its action may be deferred or neutralized by large doses of freshly precipitated ferric hydrate.

ARSENIC OXIDE AND ARSENATES.

Arsenic Oxide, As_2O_5, *Arsenic Pentoxide*, is prepared by heating arsenic acid to low redness. It forms a white, fusible, glassy mass. By a strong heat it is converted into arsenous oxide and oxygen.

Arsenic Acid, H_3AsO_4, *Orthoarsenic Acid*, is obtained by long boiling of arsenous oxide and nitric acid. The solution is evaporated to a syrupy consistence, when crystals separate having the composition $(H_3AsO_4)_2.H_2O$. These crystals deliquesce in the air, and give up their water of crystallization at 100°. On heating to 180° they lose additional water and are converted into pyroarsenic acid, $H_4As_2O_7$, and at 200° a pearly, lustrous mass of meta-arsenic acid, $HAsO_3$, is formed.

Arsenic acid has some use as an oxidizer in the preparation of a number of the aniline colors.

Sodium Arsenate, $Na_2HAsO_4.7H_2O$. **Sodii Arsenas, U. S. P.**—This official salt may be prepared by neutralizing arsenic acid with sodium carbonate, but the process given by the Pharmacopœia of 1870 is more economical; this consists in fusing together in a clay crucible 10 parts of arsenous oxide, 8.5 parts of sodium nitrate, and 5.5 parts of dried sodium carbonate. The fused product is poured while hot on a porcelain slab, dissolved in water, the solution filtered, and set aside to crystallize. The reaction involved is as follows:

$$As_2O_3 + 2NaNO_3 + Na_2CO_3 + H_2O = 2Na_2HAsO_4 + N_2O_3 + CO_2.$$

The crystals should be kept in well-stoppered bottles; they effloresce in dry air, and are somewhat deliquescent in moist air.

Properties.—Sodium arsenate occurs in colorless, transparent, monoclinic prisms. It is soluble in 4 parts of water at 15° and very soluble in boiling water; very sparingly soluble in cold alcohol, but dissolved by 60 parts of that liquid when boiling. On the application of a gentle heat the salt loses 5 molecules of

water, amounting to 28.8 per cent., at 148° the remainder of the water is given off, the salt melts, and at a red heat is converted into pyroarsenate.

Monobasic Sodium Arsenate, $NaH_2AsO_4.H_2O$, and *Tribasic Sodium Arsenate*, $Na_3AsO_4.12H_2O$, are known.

ARSENIC AND SULPHUR.

Arsenic Disulphide, As_2S_2, *Realgar*, is found native, crystallized in oblique rhombic prisms.

It is prepared by melting together 15 parts of metallic arsenic and 6.5 parts of sulphur, or by the sublimation of 4 parts arsenous oxide and 2 parts sulphur. The product occurs in red, glassy masses, translucent on the edges. It is insoluble in water, but is readily dissolved by the alkali sulphides.

Realgar is used as a coloring, in the manufacture of leather, and in the preparation of *white* or *Indian fire*. This consists of 24 parts saltpetre, 2 parts realgar, and 7 parts sulphur.

Arsenic Trisulphide, As_2S_3, *Orpiment.*—Under the latter name this compound is found in nature, crystallized in lemon-colored, rhombic prisms. It is prepared by melting together 6 parts of metallic arsenic and 4 parts of sulphur, or by subliming a mixture of 4 parts of arsenous oxide and 3 parts of sulphur. This compound is also formed when hydrogen sulphide is passed into a hydrochloric acid solution of arsenous oxide. It is melted to a yellowish-red liquid when heated, and at 700° volatilizes without decomposition.

When dissolved in the alkali sulphides it forms arsenites and thioarsenites as follows:

$$2As_2S_3 + 4KOH = KAsO_2 + 3KAsS_2 + 2H_2O.$$

On the addition of hydrochloric acid, the whole of the arsenic is reprecipitated as sulphide:

$$KAsO_2 + 3KAsS_2 + 4HCl = 2As_2S_3 + 4KCl + 2H_2O.$$

The *sulpharsenites* or *thioarsenites* constitute a class of compounds which bear the same relation to arsenic trisulphide as the arsenites bear to arsenous oxide.

Arsenic Pentasulphide, As_2S_5, is obtained by fusing arsenic trisulphide with the proper proportion of sulphur, or by precipitating a dilute solution of sodium or ammonium sulpharsenate with hydrochloric acid. It is a yellow, fusible mass which may be sublimed without decomposition, provided air is excluded.

The *thioarsenates* or *sulpharsenates* form a class of compounds, the members of which are prepared by dissolving arsenic pentasulphide in an alkali sulphide, or by precipitating an arsenate with hydrogen sulphide.

THE DETECTION OF ARSENIC IN ANIMAL TISSUES.

On account of the ease with which it may be obtained and the certainty of its action, arsenic figures in more cases of poisoning, both accidental and intentional, than any other substance.

Where some of the powdered material is obtained from the stomach in a comparatively pure form, the identification of it is quite easy. It is simply necessary to employ the usual qualitative reactions. But oftener the poison has been absorbed by the system, and it is necessary to separate it from the tissues, or it is so intimately mixed with the contents of the stomach as to make any preliminary separation impossible. The stomach and its contents, and sometimes the other organs, are cut finely and triturated in a porcelain mortar until a uniform mass is obtained. This is then placed in a clean porcelain evaporating dish, and an equal volume of hydrochloric acid, having a specific gravity of 1.12, is added. The whole is heated on a water-bath, and every five minutes from one to two grammes of potassium chlorate are added. This is continued until a thin, yellowish liquid is obtained; after the addition of a few more grammes of the chlorate, the heat is continued until all odor of chlorine has disappeared. The liquid is filtered, warmed to 70°, and treated for a considerable time with hydrogen sulphide. This sulphide may be collected, washed, dissolved, and detected by the usual arsenic reagents and tests as described in Vol. II. of this work. The method as given serves for the separation of a number of other metals that are sometimes used as poisons, and they may then be detected by the appropriate tests.

It is of the greatest importance to employ in this operation dishes and reagents that are absolutely free from the presence of traces of contamination. Therefore a blank experiment should first be carried out to prove the absence of impurities.

ANTIMONY (Stibium).

Symbol, Sb. *Atomic Weight*, 119.6. *Valence*, III and V.

History.—Although long before his time the ores of antimony, and probably the metal itself, were known to the alchemists of the East, the initiative step to the present knowledge of the element was reserved for Basil Valentine, who about the middle of the fifteenth century prepared and described not only the metal, but also a number of its compounds. At the same time he pointed out the value of the metal for the preparation of medi-

cines and of alloys. A century later, however, Libavius confounded antimony with bismuth.

In the early part of the present century, Thénard, Proust, and particularly Berzelius, added to the positive literature of this metal. The names given to the element at present are the Chaldean term, *stibium*, and the Latin title, *antimonium*, both of which were applied to the native sulphide until the time of Lavoisier.

Occurrence.—The chief source of antimony is the mineral *stibnite*, Sb_2S_3, which has been known since early history, but the metal also occurs directly combined with arsenic, nickel, and silver; and, though infrequently and in small quantities only, antimony is found in the free state associated with the preceding forms. As oxide, Sb_2O_3, we have the element occurring as octohedral crystals, *senarmontite*, and in rhombic prisms, *valentinite*. Of other antimony ores may be mentioned those in which the trisulphide, Sb_2S_3, forms thio-antimonates, or the so-called *sulphosalts*, with the sulphides of such metals as copper, iron, lead, and silver, in which arsenic often replaces part of the antimony.

Stibnite is found extensively in Canada and in Hungary; considerable antimony ore enters commerce from Cornwall, Algiers, Borneo, Nevada, South America, and New Brunswick.

Preparation.—To separate antimony from the accompanying minerals advantage is taken of the easy fusibility of the sulphide, which is heated in vertical cylinders having holes at the bottom for the egress of the molten sulphide; or this preliminary fusion is carried on in reverberatory furnaces. To obtain the metal, the purified sulphide formed as above described is either fused with metallic iron,

$$Sb_2S_3 + 3Fe = 2Sb + 3FeS,$$

or is roasted to form oxide, which is afterwards reduced with charcoal and sodium carbonate, or with crude tartar, as follows:

$$2Sb_2S_3 + 3C + 6Na_2CO_3 = 2Sb_2 + 9CO_2 + 6Na_2S.$$

The availability of the reactions of both methods was known to Basil Valentine.

The process employed in England, where much of the antimony of commerce is prepared, comprises three successive stages,—viz., "singling," which consists in melting the sulphide with one-half its weight of scrap-iron for an hour and a half in plumbago crucibles; "doubling," whereby the metallic antimony, which was separated from the slag of iron sulphide formed in the

first operation, is fused for the same time with 2.5 per cent. each of sodium sulphate and a slag consisting principally of pearl-ash; and "melting for star-metal" with a previously used slag of the last substance and an additional quantity of fresh pearl-ash for a similar period.

The metal is then poured into square moulds, its surface covered with slag, and the molten mass allowed to cool slowly to insure the peculiar crystalline structure which is required in commerce. The antimony so obtained may contain arsenic, from which it is freed by fusion with sodium carbonate and potassium nitrate, sometimes with the addition of a small quantity of antimony trisulphide, and subsequent reduction of the lixiviated mass by charcoal and sodium carbonate.

Properties.—Antimony is a lustrous, silver-white metal, more basic than arsenic but less so than bismuth. It is harder than the last metal, and like it crystallizes in obtuse rhombohedra, a mass of which exhibits a granular or a coarsely laminated, fern-marked, crystalline fracture, according as it is rapidly or slowly cooled. This structure determines the great brittleness of the metal. Antimony has a specific gravity of 6.7, is scarcely tarnished by air, melts at 432°, volatilizes at a bright red-heat, and can be distilled in hydrogen at a white-heat. On charcoal, before the blow-pipe it melts and evolves white fumes of trioxide, and, if the globule of molten metal is dropped from some height, it scatters in many small particles, which burn with a very bright flame to trioxide. At ordinary temperatures, cold water does not act upon the element, which, however, at a red-heat decomposes steam. Hot, but not cold, hydrochloric and sulphuric acids, as also cold nitro-hydrochloric acid, dissolve antimony.

Nitric acid converts the metal into white antimony trioxide, Sb_2O_3, and antimonic acid, H_3SbO_4; while solutions of the alkali hydrates produce no change. It combines directly with the halogens, and with sulphur, phosphorus, and arsenic. The existence of an amorphous allotropic modification of this element in the so-called explosive antimony obtained by the electrolysis of strong solutions of the compounds of the metal is still a matter of doubt.

Uses.—From the metal a chloride, suitable for the preparation of some of the medicinal compounds, is prepared, but the largest amount of antimony is used in the trades and manufactures in the form of alloys or of compounds. Along with bismuth, antimony finds use in the construction of thermo-electric piles.

When antimony is precipitated from a solution of the trichloride by zinc, the metal is obtained in a finely pulverulent condition. In this state it is called *antimony-black*, and is used to impart to the surface of gypsum and papier-maché figures and other objects the appearance of iron or steel.

Alloys.—These are useful because of their hardness and easy fusibility. *Type-metal* contains besides lead, and sometimes small quantities of tin, about 20 per cent. of antimony. Such an alloy expands upon cooling from the state of liquefaction, although its separate component elements when congealing shrink.

Britannia-metal consists of approximately nine parts of tin and one part of antimony, often with some addition of copper, zinc, and bismuth.

By the use of antimony superior *pewter* and *anti-friction-metal* are had; the latter is used extensively for machinery bearings, and like the former is an alloy of the metal with tin, or with tin and lead.

ANTIMONY AND HYDROGEN.

Hydrogen Antimonide (*Stibine*), SbH_3, is formed when nascent hydrogen is brought in the presence of acid into contact with finely divided antimony or any compound of it that is capable of reduction by the gas. Obtained in the usual way by the action of dilute sulphuric acid on zinc in the presence of an antimony compound, it is mixed with much hydrogen, and apparently remains unaltered for a long time; but when generated in more concentrated form by slowly adding a nearly saturated solution of antimony in strong hydrochloric acid to an excess of granulated zinc, the compound soon decomposes.

The pure gas has probably never been prepared. That yielded by the processes given is colorless, has a disagreeable smell and taste, and burns with a bluish-white or grayish flame, evolving white fumes of antimony trioxide.

If a cold porcelain plate is pressed into the flame, a sooty deposit of metallic antimony is obtained.

Hydrogen antimonide is decomposed if passed through a red-hot tube, metallic antimony being deposited close to the heated spot. If the deposit be heated the minute particles coalesce to form microscopic globules.

These metallic spots are distinguished from those produced under the same conditions by arsenic by the darker color of the former, their smoky appearance, their lesser volatility, their insolubility in hypochlorite solutions, and their solubility in ammonium sulphide.

Strong sulphuric acid decomposes the gas, as does also alkali hydrate solutions; the latter behavior accounts for the failure of antimony to produce its hydrogen compound in Fleitman's test, wherein the necessary nascent hydrogen is evolved from zinc and potassium hydrate, and whereby arsenic may be detected.

When hydrogen antimonide is conducted into a solution of silver

nitrate, a black precipitate containing silver antimonide, $SbAg_3$, and some metallic silver arising from the reduction of the silver salt by the hydrogen present, is thrown down.

ANTIMONY AND THE HALOGENS.

Antimony Trichloride, $SbCl_3$.—This was long ago prepared by subliming antimony sulphide with corrosive sublimate. It may be obtained by distilling the sulphide with hydrochloric acid, or with materials yielding it, as follows:

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

The metal or sulphide by the action of dry chlorine and heat will also furnish it.

The trichloride forms a deliquescent crystalline mass known as *butter of antimony*, which melts at 72°, and boils at 223°. The solution of the chloride (*liquid butter of antimony*) is best made by boiling the trisulphide with strong hydrochloric acid, and evaporating to remove water and excess of acid. This solution is occasionally used in medicine as a caustic; but it is extensively employed for giving a bronze surface to iron and steel wares, such, for instance, as gun-barrels. The color of the solution made from sulphide is due to ferric chloride produced from the iron present.

When the solution of the chloride is mixed with water there is thrown down an amorphous, white precipitate of the basic chloride, which, by standing in contact with the accompanying liquid, becomes crystalline.

The composition of the product varies according as it is produced by cold or hot water; the former yields SbOCl, the latter $Sb_4O_5Cl_2$; whereas the presence of free hydrochloric or of tartaric acid prevents the precipitation. These compounds were much used towards the end of the sixteenth century by a Veronese physician, Algarotus, hence the name *powder of Algaroth*, by which the dry substances are often designated.

Antimony Pentachloride, $SbCl_5$, results from the direct union of antimony and chlorine, and upon saturation of the fused trichloride with chlorine gas. It is a colorless, hygroscopic, fuming, disagreeably-smelling liquid, which solidifies at a temperature below 0°, and is decomposed by water.

This compound is used as a chlorinating agent in the preparation of certain organic chlorides.

Antimony Tribromide, $SbBr_3$.—Like chlorine, bromine combines with antimony with the evolution of light and heat. The resulting compound sublimes in colorless, deliquescent needles, which melt at 90°, boil at 275°, and are changed by water to basic bromide.

The tribromide is obtained in octohedra by heating an excess of powdered antimony with a solution of bromine in carbon disulphide and evaporating the solution.

A pentabromide is not known.

Antimony Tri-iodide, SbI_3, is a brownish-red crystalline mass obtained by directly uniting iodine and antimony with the aid of heat. It is sublimable, and altered by water, with the formation of yellow basic iodide.

ANTIMONY AND OXYGEN.

Antimony Trioxide, Sb_2O_3. **Antimonii Oxidum, U. S. P.**— As mentioned under the occurrence of antimony, this oxide is found native in the crystalline form, often colored by the presence of iron and other metals. It is isodimorphous with arsenic trioxide. A mixture of the two forms is obtained upon heating the metal to a red heat, while the octohedral variety can be produced by subliming the rhombic into which it again reverts when strongly heated.

On a small scale the oxide is usually prepared by pouring a solution of the trichloride into a boiling solution of sodium carbonate or into water. In the latter instance the precipitate of basic chloride is treated with solution of sodium hydrate to decompose it, and the resulting oxide finally washed with water, which alone is required when the use of sodium carbonate is involved in the process, the trichloride yielding oxide by reaction with that salt in the presence of hot water. In both cases the washed product is carefully dried. Antimony trioxide so prepared is "a heavy, grayish-white powder without odor or taste, and permanent in the air.

"Almost insoluble in water, and insoluble in alcohol. Nitric acid fails to dissolve it, but it is readily soluble in hydrochloric acid without effervescence, and also in a warm solution of tartaric acid, or in a boiling solution of potassium bitartrate. When heated the oxide turns yellow, becoming white again on cooling, and at a dull red heat fuses to a yellowish liquid, which concretes, on cooling, to a crystalline mass of a pearly color.

"At a higher temperature it sublimes, producing colorless and transparent, or white, shining, needle-shaped crystals."

This compound is used in the preparation of tartar emetic, which is a double tartrate of antimonyl and potassium. To a more limited extent it is itself employed in the practice of medicine, but the largest consumption of it is in painting, where it is used as a substitute for white lead. For the last purpose the oxide is prepared by roasting the metal or sulphide in air.

Antimonous Acid, H_3SbO_3, separates as a white precipitate when weak sulphuric or nitric acid is cautiously added to tartar emetic solution. When dry it is a fine, white powder.

Metantimonous Acid, $HSbO_2$, is obtained as a white, amorphous precipitate when antimony trichloride is decomposed with a solution of potassium hydrate or carbonate, in the former of which, when applied in excess, it redissolves. Hot water de-

composes it into trioxide. With alkalis it acts the part of an acid, although it saturates acids to give salts of antimony containing the group, SbO, usually termed *antimonyl*.

Antimony Tetroxide, Sb_2O_4.—This has been regarded as composed of both antimony trioxide and antimony pentoxide, for the reason that when treated with tartaric acid solution the former is dissolved while the latter remains. The structural formulas proposed are $Sb_2(SbO_4)_2$ and $(SbO)SbO_3$; the first would be called antimony antimonate, the second antimonyl metantimonate. This substance results when either of the other oxides is ignited. When heated it becomes yellow, but when cold it is white. When heated with potassium hydrate a compound known as potassium hypoantimonate, and having the formula $K_2Sb_2O_5$, is left upon washing out the fused mass with cold water.

Antimony Pentoxide, Sb_2O_5, is obtained by heating antimonic acid or by evaporating the metal, or trioxide, with nitric acid and gently heating the residue. It is a yellowish, tasteless powder, which is soluble in hydrochloric acid, but not in water. Like arsenic oxide, it forms hydrates which have acid characters. They are antimonic acid, H_3SbO_4, pyroantimonic acid, $H_4Sb_2O_7$, and metantimonic acid, $HSbO_3$. The second of those named is usually termed metantimonic acid, and the last antimonic acid, but that their relationship to the acids of arsenic may be more readily seen, the names applied to the latter are used here.

Antimonic Acid, H_3SbO_4, is produced when antimony pentachloride is added by drops to cold water. Thus obtained it is a gelatinous precipitate possessing a metallic, astringent taste and a distinct acid reaction.

At 100° it loses water, and is changed to pyroantimonic acid, $H_4Sb_2O_7$, which is more soluble in water than antimonic acid. It also dissolves in ammonium hydrate, forming ammonium pyroantimonate, $(NH_4)_4Sb_2O_7$, which exists only in solution.

Potassium Pyroantimonate, $K_4Sb_2O_7$, is obtained by fusing the gelatinous metantimonate with three times its weight of potassium hydrate, dissolving the fused mass in water, and evaporating. It is not stable.

The *Acid Sodium Salt*, $Na_2H_2Sb_2O_7 + 6H_2O$, is remarkable as being the only insoluble compound of sodium, and its formation is sometimes used as a test for that element, but necessarily only in the absence of other metals.

Metantimonic Acid, $HSbO_3$, remains when pyroantimonic acid loses water at 200°, or when powdered antimony is evaporated

with nitric acid and the residue washed. It is also formed by evaporating the potassium salt with excess of nitric acid and washing the product so obtained. It is a white, infusible powder, which is insoluble in water, but soluble in tartaric and hydrochloric acids.

Potassium Metantimonate, $2KSbO_3 + 5H_2O$, is prepared by deflagrating metallic antimony or the trisulphide with potassium nitrate. Upon lixiviation with warm water there is left a white powder, which, when boiled for some time with water, dissolves to a considerable extent.

A crystalline or a gummy mass separates from this solution, according as it is moderately or in large part evaporated.

By substituting sodium nitrate for the potassium salt, sodium metantimonate may be procured.

A basic lead metantimonate is used in oil-painting, under the name of *Naples yellow*, and is produced by heating a mixture of one part of tartar emetic, two parts of lead nitrate, and four parts of sodium chloride for two hours to the fusing point of the last-named ingredient, and subsequently washing out the soluble part with water.

Antimony Trisulphate, $Sb_2(SO_4)_3$, forms white masses of crystals as the product of the action of strong sulphuric acid on antimony or its trioxide. The compound is decomposed by water.

ANTIMONY AND SULPHUR.

Antimony Trisulphide, Sb_2S_3, **Antimonii Sulphidum**, U. S. P., occurs native as the most important ore of antimony. Though occasionally found crystallized in prisms, it usually forms columnar or striated masses, which soil the fingers like graphite. The native sulphide is purified by fusion, whereby it is separated from the associated mineral matter. The product, crude sulphide of commerce, consists of "steel-gray masses of a metallic lustre and a striated, crystalline fracture," which are easily pulverized and fused.

This article is likely to contain arsenic, which is almost completely separated by macerating the finely-divided substance with about one-half its weight of 10-per-cent. ammonium hydrate solution, which dissolves the impurity from out the antimony compound, and leaves the **Antimonii Sulphidum Purificatum**, U. S. P.

When this purified sulphide is boiled with about twelve times

its weight of 5-per-cent. sodium hydrate solution for two hours, the following reaction takes place :

$$2Sb_2S_3 + 4NaOH = NaSbO_2 + 3NaSbS_2 + 2H_2O.$$

If the solution thus obtained is strained, and while still hot decomposed by excess of diluted sulphuric acid, an amorphous, reddish-brown powder is thrown down :

$$NaSbO_2 + 3NaSbS_2 + 2H_2SO_4 = 2Sb_2S_3 + 2H_2O + 2Na_2SO_4.$$

When collected, washed, and dried at a slightly elevated temperature, the powder is found to be odorless and tasteless.

It is known in medicine as sulphurated antimony, **Antimonium Sulphuratum,** U. S. P., or *kermes mineral,* and formerly was much used as a remedy.

A very small amount of trioxide contaminates the above product. Artificial trisulphides may be produced by melting antimony with sulphur, or by precipitating a solution of an antimony salt with hydrogen sulphide. The amorphous, orange, hydrated product of the last method may be changed to the crystalline black trisulphide by heat.

Uses.—Crystalline antimony trisulphide is used not only for the preparation of the other antimony compounds, but also in fireworks, such as the *blue* or *Bengal lights* used at sea, and for the preparation, especially in Sweden, of the heads of *lucifer-matches*, as well as for the composition of percussion-caps. The amorphous variety is largely used as a means for vulcanizing caoutchouc, to which it imparts a reddish-brown color.

Antimony Pentasulphide, Sb_2S_5, sometimes called *golden sulphuret of antimony*, cannot be prepared by the direct combination of its constituent elements, but can be obtained by boiling the trisulphide and sulphur with fixed alkali hydrate or carbonate and subsequent neutralization of the solution by acid.

It may also be had as a fine yellowish-red powder by acidifying a solution of a crystallized sulphantimonate. The resulting precipitate, when carefully dried in the dark, is easily soluble in aqueous solutions of alkali hydrates and sulphides.

Antimony Cinnabar is an oxysulphide obtained by the action of a solution of sodium thiosulphate upon antimony trichloride. It is used in painting. *Crocus* and *glass of antimony* consist of varying proportions of oxide and oxysulphide, and are gotten by partly roasting the ore in air, or by incomplete oxidation by deflagration with potassium nitrate.

Both tri- and pentasulphide of antimony are capable of combining with the alkali sulphides to form sulphantimonites and sulphantimonates respectively. Acids corresponding to these salts are not known in the free state, but the salts themselves have been studied. The alkali sulphantimonites, which are brown or black, are produced by fusing the alkali hydrate or carbonate with antimony trisulphide, or by dissolving the latter in a solution of an alkali hydrate whereby both sulphantimonite and antimonite are formed. The solutions are not stable, but are decomposed by acids with precipitation of the amorphous trisulphide.

This class of compounds is sometimes called *liver of antimony*.

Sodium Sulphantimonate, $Na_3SbS_4 + 9H_2O$, or *Schlippe's Salt*, is the best representative of the higher class of these sulpho-salts. It is prepared by heating a mixture of 8 parts of anhydrous sodium sulphate and 3 parts of charcoal to fusion in a crucible, and adding thereto, under continued heat, 6 parts of finely-powdered antimony trisulphide previously mixed with 1½ parts of sulphur, maintaining the fusion until the color of the trisulphide has disappeared. The cooled mass is extracted with water.

The same compound may also be made in the wet way by boiling the trisulphide and sulphur with milk of lime and sodium carbonate.

In both cases the filtered solutions are evaporated and allowed to crystallize. The salt is obtained in fine, transparent tetrahedra which are soluble in three parts of water. When the solution is acidified antimony pentasulphide is thrown down.

Schlippe's salt is used in photography.

The sulphantimonates of the heavy metals are insoluble in water, and can be formed by double decomposition of the proper substances. They include many of the ores of antimony.

Antimony Triselenide, Sb_2Se_3, and pentaselenide, Sb_2Se_5, antimony tritelluride, Sb_2Te_3, antimony phosphide, SbP, and antimony arsenide, Sb_2As_3, are known; the last as an ore of the metal, the others as products of the union of the elements.

BISMUTH.

Symbol, Bi. *Atomic Weight*, 208.9. *Valence*, III and V.

History.—Probably bismuth was first distinctly recognized in 1450 by Basil Valentine, who attempted to classify it with other metals. In the following century, Paracelsus classed it among

the *semi-metals*, but it was afterwards proposed as a true metal by Agricola. Although clearly described by the last author, bismuth was subsequently confounded with other metals, especially with antimony and zinc, until 1739, when Pott contributed to the more accurate knowledge of the element. Its reactions were investigated by Bergman.

The name is from the German, *Wismuth*.

Occurrence.—The sources of bismuth are not numerous. It forms an exception to most metals by occurring chiefly in the free state, sometimes nearly pure. Both the metal and its ores are generally disseminated through rock. The most important works for its production are at Schneeberg, in Saxony, where the ore occurs associated with cobalt minerals. The mines of England, France, Hungary, and Scandinavia also afford it.

The Magnesium Works at Patricroft, in England, work up considerable quantities of imported bismuth ore, which in recent years has been brought into commerce from California, Colorado, Utah, Texas, Mexico, South America, and Australia.

Besides as native metal, bismuth is found as *bismuth-ochre*, Bi_2O_3, less frequently as *bismuthite*, Bi_2S_3, and occasionally associated with many of the heavy metals and as carbonate and silicate.

Preparation.—The process of obtaining the metal usually applied in the past consisted in heating the ore in iron tubes inclined in such a way that the easily fusible metal could run off into proper receptacles. This method extracted only that part of the bismuth which existed in the free state.

At present the ores are roasted to expel most of the sulphur, and then fused in small furnaces with iron to remove sulphur, charcoal to reduce the ore, and slag to facilitate the operation. The molten mass so obtained is allowed to stand, when a separation into two layers occurs, the lower being nearly pure bismuth. When the upper layer, which consists of the cobalt-speiss, iron, and various constituents of the ore, has hardened, the still liquid bismuth is transferred to ingot moulds.

When the metal occurs in ores of lead and silver, it is extracted from the slag, in which it collects in quantity from 5 to 20 per cent., by cold hydrochloric acid, and subsequently precipitated as basic chloride by water, or as metal by means of iron. In all such cases it is finally reduced by soda-ash and coal.

Bismuth is generally sent into commerce in hemispherical masses which weigh from 10 to 12 kilogrammes.

Properties.—Bismuth is isomorphous with arsenic and antimony. It is generally met with in brilliant, grayish-white or iridescent masses having a crystalline lamellate texture, on account of which, although hard, the metal can be readily reduced to a powder. The roseate tinge usually present is said to arise from a slight superficial oxidation. When melted and allowed to cool the metal expands quite notably.

Bismuth is the most diamagnetic of all known bodies, a good conductor of electricity, but a poor conductor of heat. It combines directly with the halogens and sulphur, and has a specific gravity of 9.83.

It melts at 264°, and at a white heat (about 1100°) may be distilled in hydrogen. It is permanent in air at ordinary temperatures, but when heated before the blowpipe on charcoal yields bismuth trioxide as a brown incrustation, which becomes yellow on cooling.

Hydrochloric acid does not dissolve the metal, but it is soluble in nitrohydrochloric acid and in hot concentrated sulphuric acid. Nitric acid also dissolves bismuth. When an acid of specific gravity 1.2 is employed, the presence of arsenic may be detected by the white deposit of bismuth arsenate, which fails to dissolve.

Although commercial bismuth is likely to contain arsenic and other impurities, still it is usually found in the market of such purity that it can be used for preparing the compounds, particularly the basic nitrate, and some authorities state that the presence of as much as .5 per cent. of arsenic does not disqualify the metal for that purpose.

To free it of arsenic the powdered metal is mixed with 5 or 6 per cent. of potassium or sodium nitrate and fused in a Hessian crucible by means of a charcoal fire. After the half-cooled mass has been heated for a minute with 5 per cent. fixed alkali hydrate solution, the metal is collected and thoroughly washed with water.

Other processes of purification consist in fusing the bismuth with potassium bitartrate in a carbon crucible, or with potassium carbonate, charcoal, and soap.

Uses.—Large quantities of bismuth are used for preparing its compounds, especially the subnitrate, and for alloys.

Alloys.—The presence of bismuth materially lowers the fusing point of alloys, and on that account, as also because of its property of expanding when fused and allowed to cool, alloys containing it are specially adapted

for type-metal, for taking the impression of wood-cuts, and for stereotyping. For the last two purposes the so-called *fusible metals* are employed. Of these, *Wood's metal*, consisting of 15 parts of bismuth, 8 parts of lead, 4 parts of zinc, and 3 parts of cadmium, melts at 68°, while *Rose's Metal*, containing 1 part of tin, 1 part of lead, and 2 parts of bismuth, has a fusing point of 94°. Many other uses are made of its alloys.

BISMUTH AND THE HALOGENS.

Bismuth Dichloride, $BiCl_2$ or Bi_2Cl_4, is formed when a slow current of chlorine is passed over the fused metal, or when the latter is heated with calomel to 250°. It is a black, crystalline mass, readily decomposed.

Bismuth Trichloride, $BiCl_3$, is obtained when bismuth is heated in dry chlorine, or by distilling 1 part of finely-divided metal with 2 parts of mercuric chloride, and also by dissolving bismuth in nitro-hydrochloric acid, evaporating the solution, and distilling the residue.

It is a white, deliquescent, fusible, and volatile mass, known as *bismuth butter*. It is soluble in alcohol, and by the addition of much water is changed to insoluble, white, crystalline basic bismuth chloride, known as *pearl white*.

Bismuth trichloride forms double chlorides with the alkali metals.

Bismuth Tri-iodide, BiI_3, results from the direct combination of its constituent elements when the same are fused together, but it may be more conveniently prepared by precipitation of a solution of bismuth nitrate by potassium iodide. So obtained it is a brown-red powder.

Bismuth Oxyiodide, BiOI.—This compound is produced by boiling for half an hour a solution of 40 parts of bismuth subnitrate in 3 parts of nitric acid and 400 parts of water with 24 parts of potassium iodide dissolved in 200 parts of water.

The very fine crystalline precipitate is collected, washed, and dried below 100°.

Uses.—This substance has been proposed in late years as a substitute for iodoform.

BISMUTH AND OXYGEN.

The compounds of bismuth form two classes : those in which the metal, as such, is in combination with the negative atom or group of atoms, and those wherein the univalent group, BiO, known as *bismuthyl*, occupies the same position.

Bismuth Trioxide, Bi_2O_3, the most important of this class of compounds, occurs naturally as *bismuth-ochre*. It may be prepared by heating bismuth or its carbonate, nitrate, or hydrate, and is usually seen in the form of a yellow, fusible powder, or as small needles of the same color.

It is insoluble in water, and constitutes a stronger base than antimony trioxide. Strong acids dissolve it to form corresponding salts of bismuth.

Bismuth trioxide is employed in the manufacture of optical glass, to which it imparts greater hardness and higher refractive power than is obtained by the use of lead.

Bismuth Dioxide, Bi_2O_2, *Bismuth Tetroxide*, Bi_2O_4, and *Bismuth Pentoxide*, Bi_2O_5, are known.

Bismuthyl Hydrate, $BiO(OH)$, is produced when a solution of bismuth nitrate in nitric acid is slowly added to a cold solution of sodium hydrate. It is a white, amorphous powder, and has weak basic properties.

Bismuth Trihydrate, $Bi(OH)_3$.—When a solution of a bismuth salt is treated with an excess of cold ammonium hydrate, this compound is obtained as a white precipitate. It has the characters of a base, and upon heating is converted into bismuth trioxide.

Of the more acid hydrates, that having the composition $BiO_2(OH)$ is formed by passing chlorine into potassium hydrate solution in which bismuthyl hydrate has been suspended, while $Bi_2O_3(OH)_4$ is obtained by the action of potassium cyanide on bismuth nitrate.

OXYGEN SALTS OF BISMUTH.

Bismuth Nitrate, $Bi(NO_3)_3.5H_2O$, is obtained by gradually adding to 5 parts of nitric acid of specific gravity 1.2 contained in a capacious flask, and previously heated to from 75° to 90°, 1 part of coarsely-powdered bismuth. A strong reaction ensues, the metal is dissolved and nitrogen dioxide is liberated. On account of this gas changing in the air to noxious nitrogen tetroxide, the operation is best conducted in a place capable of ventilation:

$$2Bi + 8HNO_3 = 2Bi(NO_3)_3 + 4H_2O + 2NO.$$

When the solution has been filtered through asbestos to remove bismuth arsenate, evaporated, and allowed to cool, the salt crystallizes, while the impurities remain in the mother-liquor.

Bismuth nitrate forms colorless, transparent, columnar masses which melt at 73° in their water of crystallization, and which by continued heating at 80° lose water and nitric acid, and are changed to a white basic nitrate. It dissolves in a small quantity of water to form a strongly caustic liquid, which, upon the further addition of water, is precipitated through the production of white basic nitrate, in which the proportion of the nitric acid radical is much decreased.

From this salt most of the useful salts of the metal are prepared.

Basic Bismuth Nitrate, $(BiO)NO_3.H_2O$. **Bismuthi Subnitras**, U. S. P.—This compound was introduced into the practice of medicine by Odier in 1786.

It is "a heavy, white powder, of somewhat varying chemical composition, odorless and almost tasteless, and permanent in the air. Almost insoluble in water, and insoluble in alcohol; but readily soluble in nitric and hydrochloric acids. When heated to 120° C., the salt loses water (between 3 and 5 per cent. of its weight); and when subsequently heated to redness, it evolves nitrous vapors, leaving from 79 to 82 per cent. of its weight of a yellow residue which is soluble in nitric or hydrochloric acid, and blackened by hydrogen sulphide. When brought upon moistened blue litmus paper, the salt shows a slightly acid reaction."

The composition of the salt depends upon the quantity and temperature of the water employed for precipitation and washing and the rapidity with which the process of preparation is conducted.

The official product described above may be obtained by the following method: 1 part of bismuth nitrate and 4 parts of water are thoroughly rubbed together, and the mixture during stirring is poured into 21 parts of boiling water, which react as follows:

$$Bi(NO_3)_3 + 2H_2O = (BiO)NO_3.H_2O + 2HNO_3.$$

When the precipitate has subsided, the still warm supernatant liquid is poured off, the precipitate is collected on a filter and, after the filtrate has ceased to drop, is washed with an equal volume of cold water. After a repetition of the washing, the precipitate is pressed and dried at a temperature not above 30°. On account of the acid present, the liquid from which the precipitate has been collected retains not inconsiderable amounts of bismuth nitrate, the greater part of which can be thrown down as basic nitrate, if the solution be nearly neutralized with sodium hydrate. This is usually collected, washed, and added to the first precipitate. From the filtrate the remaining traces of bismuth may be recovered as basic carbonate or as hydrate by the addition of an excess of sodium carbonate or of ammonium hydrate respectively.

100 parts of crystallized bismuth nitrate yield about 60 parts of bismuth subnitrate.

Uses.—Besides its use in medicine, bismuth subnitrate is extensively employed in cosmetics under the name of *flake-white*, and in the preparation of a colorless, iridescent glaze for porcelain and in glass staining.

Basic Bismuth Carbonate, $(BiO)_2CO_3.H_2O$. **Bismuthi Subcarbonas**, U. S. P., is "a white or pale yellowish-white powder, of somewhat varying chemical composition, odorless and tasteless, and permanent in the air. Insoluble in water or alcohol, but completely soluble in nitric or hydrochloric acid, with copious effervescence. When heated to redness, the salt loses water and carbon dioxide, and leaves from 87 to 91 per cent. of a yellow residue which is soluble in nitric or hydrochloric acid, and blackened by hydrogen sulphide."

It is prepared by pouring a solution of bismuth nitrate into a cold solution of sodium carbonate.

Another basic carbonate is found native in small quantity as

a yellow amorphous mass. Neutral bismuth carbonate is not known. The artificial salt is used in medicine.

The three elements just considered, Arsenic, Antimony, and Bismuth, according to the periodic system (see p. 346), belong in the same group with Nitrogen and Phosphorus. As supplementary to this group and forming a related sub-group we have Vanadium, Niobium (or Columbium), and Tantalum.

VANADIUM.

Symbol, V. *Atomic Weight*, 51.1. *Valence*, III and V.

Vanadium occurs chiefly as the vanadates of lead and copper in Cheshire, England, and other localities. It is obtained as a whitish-gray colored metallic powder by the reduction of the dichloride by hydrogen. Its sp. gr. at 15° is 5.5. With oxygen it forms five oxides corresponding to the oxides of nitrogen. The first three, or lowest of these, act as basic oxides, and the two highest act as acid-forming oxides.

Vanadium Pentoxide, V_2O_5, or vanadic anhydride, is a brown mass obtained by fusing the naturally occurring vanadates with nitre. It dissolves in the alkalies, forming the normal *vanadates*. The free acid, H_3VO_4, is not known, but salts, such as Na_3VO_4, exist. The *metavanadic acid*, HVO_3, forms a fine yellow pigment sometimes termed "vanadium bronze." The most important salt of this acid is *ammonium metavanadate*, NH_4VO_3. The solution of this salt becomes deep black when treated with tincture of galls. As the solutions containing this highest oxide of vanadium are reduced they show very characteristic changes of color: thus, vanadic salts are yellow; hypovanadic salts blue; vanadous salts green; and hypovanadous salts lavender colored.

Vanadium forms three chlorides, VCl_4, VCl_3, and VCl_2, and a number of oxychlorides such as $VOCl_3$, $VOCl_2$, and VOCl.

NIOBIUM (or Columbium).

Symbol, Nb (or Cb). *Atomic Weight*, 93.7. *Valence*, III and V.

Niobium, as it was named by Rose, or Columbium, as it was first named by Hatchett, is a very rare metal found in columbite and tantalite and other rare minerals. Niobium has been obtained as a steel-gray crust of sp. gr. 4.06. Its most important compound is $HNbO_3$, forming salts known as *niobates*.

TANTALUM.

Symbol, Ta. *Atomic Weight*, 182. *Valence*, III and V.

Tantalum accompanies niobium in the minerals above named. It has been obtained as an iron-gray powder. Its most important compound is *tantalic acid*, $HTaO_3$, which forms *tantalates*.

CHAPTER IX.

THE CHROMIUM GROUP.

CHROMIUM.

Symbol, Cr. *Atomic Weight*, 52. *Valence*, II, $(Cr_2)^{VI}$ and VI.

CHROMIUM was discovered by Vauquelin in 1797. Klaproth, independently, and about the same time, made the same discovery. Both chemists first observed it in the mineral *crocoisite*, a lead chromate.

Chromium is not found in the free state in nature ; its compounds are neither abundantly nor widely distributed. The best-known occurrence is as chrome iron ore, or *chromite*, FeO,Cr_2O_3. This is found in the Shetland Islands, in Norway, and in the Urals. In the United States it is found near Philadelphia, in beautiful octohedral crystals, and at the chrome mines in Lancaster County, Pennsylvania. Maryland also yields some chrome ore. The chief supply in this country comes from California at the present time.

Preparation.—Chromium is obtained in the metallic state by reducing the chloride with zinc. For this purpose chromic chloride is heated in a Hessian crucible with metallic zinc, a mixture of potassium and sodium chlorides being added as a flux. The resulting metallic button is a mixture of chromium and zinc, from which the latter is dissolved by treatment with dilute nitric acid so long as anything is dissolved. The metallic chromium is left behind as a gray powder. When chromic oxide is heated to whiteness with charcoal the metal is obtained.

Properties.—Chromium, when prepared by reduction with zinc, is a light-gray, crystalline, non-magnetic powder, which is seen by the aid of a microscope to consist of minute rhombohedra. It is highly infusible, and is not easily oxidized in the air. Hydrochloric acid dissolves the metal rapidly, with evolution of hydrogen ; diluted sulphuric acid, when hot, behaves in a similar manner, but concentrated nitric acid does not attack it.

Uses.—Chromium in the proportion of 0.5 to 0.75 per cent. is employed to impart hardness to steel, and its ore is used in increasing amount in furnace lining in the iron manufacture.

CHROMIUM AND THE HALOGENS.

Chromous Chloride, $CrCl_2$.—When hydrogen is passed over warmed chromic chloride the chromous salt is obtained as a white, crystalline mass. It dissolves in water, forming a blue solution; this solution rapidly absorbs oxygen, and acts as a powerful reducing agent.

Chromic Chloride, Cr_2Cl_6, is prepared by forming sticks of equal parts of chromic oxide and charcoal, by the aid of mucilage of starch, and burning them, then heating them in porcelain tubes to strong redness and leading in a current of dry chlorine. The product is in reddish-violet, lustrous scales, which are nearly insoluble in water, but readily dissolve in that liquid with a green color in the presence of a trace of chromous chloride. Chromic chloride may be obtained in solution by dissolving chromic hydrate in hydrochloric acid; by concentrating this solution very slowly, easily soluble crystals, having the composition $Cr_2Cl_6.12H_2O$, separate.

Chromous Bromide, $CrBr_2$, and *Chromic Bromide*, Cr_2Br_6, are prepared like the corresponding chlorides.

CHROMIUM AND OXYGEN.

Chromous Oxide, CrO.—This oxide is not known in the anhydrous state, but *chromous hydrate*, $Cr(OH)_2$, is easily formed by precipitating chromous chloride with potassium hydrate; it forms a brown precipitate, which oxidizes so readily that air must be excluded in order to obtain it in anything like a state of purity.

Chromium Sesquioxide, Cr_2O_3, *Chromic Oxide*, occurs native, mixed with clay, as *chrome-ochre*. It may be prepared in a pure condition by heating to redness chromic hydrate and some other chromium compounds. It is a dark-green, amorphous powder, which fuses in the oxy-hydrogen flame, and solidifies to a black, crystalline mass. It may be obtained in lustrous, dark-green, hexagonal crystals by passing the vapor of chromic oxychloride through a red-hot porcelain tube.

Chromic oxide is used in the preparation of colored glass, enamels, and porcelain, to which it imparts a beautiful green tint. It is known in commerce as *chrome green*. *Guignet's green* is a hydrate obtained by heating a mixture of potassium dichromate and boric acid, and extracting with water.

Chromic Hydrate, $Cr_2(OH)_6$, is formed as a voluminous bluish-green precipitate, when ammonia water is added to a solution of chromic salt. When the compound is dried over sulphuric acid at ordinary temperatures it has the composition $Cr_2(OH)_6.4H_2O$. The water may be driven off at 100°.

Chromium Trioxide, CrO_3. **Acidum Chromicum, U. S. P.** *Chromic Anhydride*, *Chromic Acid*.—This compound was first prepared in 1797 by Vauquelin. It is best obtained by adding

to 1 volume of a saturated solution of potassium bichromate 1½ volumes of concentrated sulphuric acid:

$$K_2Cr_2O_7 + 2H_2SO_4 = 2CrO_3 + 2KHSO_4 + H_2O.$$

By cooling, the oxide is caused to separate in acicular crystals; these are drained in a funnel, then pressed between porous bricks, again placed in the funnel and washed with nitric acid having a specific gravity of 1.46. After the nitric acid has drained off, the crystals are pressed between porous bricks a second time and dried on a sand-bath until no more nitrous fumes can be detected. Another method of purification consists in repeatedly crystallizing the chromium trioxide from a small quantity of water, and removing the last traces of sulphuric acid by the addition of a little barium chromate.

Properties.—Chromium trioxide occurs in lustrous, brownish-red, acicular crystals or rhombic prisms, having a specific gravity of 2.8. The crystals are very soluble in water, and deliquescent in moist air. The scarlet-red crystals usually contain sulphuric acid, while those that are purified from this substance are darker, with a brownish-red color and a steel-blue lustre. On account of its energetic oxidizing action the oxide cannot be brought in contact with the usual organic solvents, as they are liable to be inflamed thereby. In fact, it must be preserved in glass-stoppered bottles, and not brought in contact with such substances as cork, tannin, sugar, alcohol, etc. "When Chromic Acid is heated, its color darkens, and finally becomes black, but is restored on cooling. At 192° to 193° it fuses to a reddish-brown liquid, which, on cooling, forms a dark-red, brittle mass (often enclosing cavities filled with crystals), furnishing a scarlet powder." After protracted heating at 250° it is entirely decomposed into chromic oxide, Cr_2O_3, and oxygen.

Uses.—Chromium trioxide is employed medicinally as a caustic, in dilute solution (1 to 100) for hardening tissues in microscopic preparations, and more extensively as an oxidizing agent in the laboratory.

Chromium Oxychloride, Chromyl Chloride, CrO_2Cl_2, is obtained by introducing a fused mixture of 10 parts of common salt and 12 parts of potassium dichromate in small pieces into a retort with 30 parts of concentrated sulphuric acid. The retort must be connected with a well-cooled receiver, as the reaction proceeds without the aid of heat, a dark-red, nearly black, liquid distilling over. It has a specific gravity of 1.97 at 25°, and boils at 118°.

CHROMIC ACID AND CHROMATES.

Chromic Acid, H_2CrO_4.—This acid is analogous to sulphuric acid. It is prepared by adding to chromium trioxide a little less water than is required to form H_2CrO_4; the mixture is heated to 100°, the clear solution decanted and cooled to 0°, when small, red, acicular crystals are deposited. These crystals are dried over sulphuric acid at the ordinary temperature, and are then found to have the composition H_2CrO_4; they are very hygroscopic.

Potassium Chromate, K_2CrO_4. *Neutral* or *Yellow Potassium Chromate.*—In order to prepare this salt, 2 parts of potassium dichromate are dissolved in 4 parts of hot water, to the resulting solution about 1 part of potassium carbonate is added, or such an amount as will produce a weak alkaline reaction :

$$K_2Cr_2O_7 + K_2CO_3 = 2K_2CrO_4 + CO_2.$$

After filtering the yellow solution and concentrating, yellow crystals separate.

Properties.—Potassium chromate occurs in permanent, yellow, rhombic crystals, which are isomorphous with potassium sulphate. The salt is soluble in 2 parts of cold water, forming a yellow solution which has a weak alkaline reaction towards litmus paper. It is insoluble in alcohol. The aqueous solution is colored red on the addition of acids, owing to the formation of the dichromate.

Potassium chromate is useful as a reagent.

Potassium Dichromate, $K_2Cr_2O_7$. **Potassii Bichromas, U. S. P.** *Potassium Bichromate.*

Preparation.—This salt is made from chrome iron ore by fusing in a reverberatory furnace with potassium carbonate and nitrate, or a more recent method consists in heating the chrome ore, then powdering, and making an intimate mixture of the ore 2 parts, calcium oxide 3 parts, and potassium carbonate 1 part; this mixture is heated to redness in a reverberatory furnace. The result is a greenish-yellow mixture of iron and calcium oxide, calcium chromate and potassium chromate; the two salts of chromium are washed out with water. The calcium chromate is converted into potassium chromate by the addition of potassium carbonate or sulphate. The solution of potassium chromate is treated with sulphuric acid according to the following reaction :

$$2K_2CrO_4 + H_2SO_4 = K_2Cr_2O_7 + K_2SO_4 + H_2O.$$

The potassium sulphate is used in converting another portion of calcium chromate. Potassium dichromate is purified by crystallization from five times its weight of hot water.

Potassium dichromate crystallizes in red, anhydrous, triclinic prisms or four-sided tables. It is permanent in the air, odorless, and has a bitter, metallic taste. The salt is soluble in 10 parts of cold water, in 1.5 parts of boiling water, but insoluble in alcohol. The aqueous solution is acid to litmus paper. On the application of heat it fuses without loss of weight, and at a white heat oxygen is evolved, leaving a residue of neutral potassium chromate and green chromic oxide.

Uses.—Potassium dichromate is rarely employed in medicine. It is, however, extensively used in the dyeing and tanning industries, and in a number of smaller operations.

Sodium Chromate, Na_2CrO_4, and *Dichromate*, $Na_2Cr_2O_7$, are prepared similarly to the potassium salts. The chief difficulty appears to be in the crystallization of the sodium salt. According to Walberg, the following process gives satisfactory results: 6 parts of finely-ground chrome ore (containing 44 per cent. of Cr_2O_3) are intimately mixed with 3 parts of soda-ash (containing 92 per cent. sodium carbonate) and 3 parts of chalk. The whole is strongly heated in the oxidizing flame of a reverberatory furnace, the charge of the furnace being one ton. The hot mass is lixiviated with water, forming a liquid of 84° Tw. It is then concentrated in an iron pan to 104° Tw., and run into tanks lined with lead, where acicular crystals separate, having the composition $Na_2CrO_4.10H_2O$. These are drained by a centrifugal machine, then placed in a well-ventilated chamber, heated to 30°, where they effloresce and crumble to a yellow, anhydrous powder. The dichromate is prepared from this similarly to the potassium salt. It occurs in deliquescent crystals, which are used in many technical processes in place of potassium dichromate, because of their more ready solubility in cold water.

Barium Chromate, $BaCrO_4$, is a yellow powder, insoluble in water and in acetic acid. It is obtained by precipitation of a soluble barium salt with potassium chromate or dichromate. Under the name of *yellow ultramarine* it is used as a pigment.

Lead Chromate, $PbCrO_4$.—There are at least three commerical substances which belong under this title,—namely, the neutral chromate, or *chrome yellow*, basic chromate, or *chrome red*, and *chrome orange*, which is a mixture of the two.

Chrome yellow is prepared by precipitating a solution of potassium chromate with a solution of lead acetate. The precipitate is often mixed with gypsum or barium sulphate in order to obtain the lighter chrome colors. Another process consists in digesting lead sulphate, which is a by-product in many calico-printing and

dye-works, with a solution of potassium chromate. The depth of shade depends upon the amount of unchanged lead sulphate. It is stated that a beautiful chrome yellow may also be obtained by digesting 100 parts of freshly-precipitated lead chloride with 47 parts of potassium dichromate.

Chrome red is a basic lead chromate having the composition $PbCrO_4, Pb(OH)_2$. It is sometimes known as *Austrian cinnabar*. In order to obtain it the yellow chromate is boiled with a solution of potassium hydrate, or a better quality is made by fusing together equal parts of sodium and potassium nitrates, and adding to the fused mass, in small quantities at a time, the yellow chromate. After cooling, the insoluble chrome red is well washed and dried. The different shades of this compound appear to be due to the size of the crystalline particles, as may be shown by separately rubbing a number of samples to a uniform powder.

A large number of other chromates are known, and may in most cases be prepared by precipitating a soluble salt of the metal with potassium dichromate.

OXYGEN SALTS OF CHROMIUM.

Chromous Sulphate, $CrSO_4.7H_2O$, is prepared by cooling a solution of chromous acetate in dilute sulphuric acid, whereby crystals of the above composition separate. It is also obtained when metallic chromium is dissolved in dilute sulphuric acid. When concentrated sulphuric acid is added in excess to the above solution, a white salt having the composition $CrSO_4.H_2O$ is precipitated.

Chromous sulphate occurs in bluish crystals, which are isomorphous with magnesium sulphate.

Chromic Sulphate, $Cr_2(SO_4)_3.18H_2O$.—This compound is prepared by dissolving chromic hydrate in the necessary quantity of dilute sulphuric acid. The crystals may be obtained by careful evaporation or by the addition of alcohol. The solution is green when first prepared, but becomes violet on standing, and deposits crystals of a violet color.

When the violet-colored solution is boiled for some time it becomes green, and is then not precipitated by alcohol, and yields an amorphous, green mass by evaporation; but by long standing the solution again becomes violet, and will then yield the normal salt either by evaporation or by precipitation with alcohol.

It is probable that the boiling causes the formation of a basic salt.

Chromium and Potassium Sulphate, $K_2Cr_2(SO_4)_4.24H_2O$, *Chrome Alum*.—This salt is obtained by dissolving in water molecular proportions of chromic sulphate and potassium sulphate and carefully evaporating. The violet-red solution yields dark crystals of the same color as the solution from which they separate, having the above composition. It may also be prepared by adding to an aqueous solution of potassium

dichromate the necessary quantity of sulphuric acid and passing in sulphurous oxide. When the solution is heated it turns green, and crystals cannot be obtained from it, but by long standing it acquires the violet-red color and will then crystallize.

Other alums of chromium may be obtained by the substitution of the sulphates of ammonium or sodium.

Chrome alum is obtained commercially as a by-product in the manufacture of certain aniline dyes. It is used as a mordant in dyeing, and to some extent in the manufacture of leather.

Chromic Nitrate, $Cr_2(NO_3)_6$, is obtained by dissolving chromic hydrate in nitric acid. The resulting solution is blue by transmitted light and red by reflected light, and the crystals which are deposited have a purple-red color.

Chromic Phosphate, $Cr_2(PO_4)_2$, is made by adding to chromic chloride a solution of sodium phosphate. It is obtained as a green precipitate, which becomes blue on drying.

MANGANESE.

Symbol, Mn. *Atomic Weight*, 54.8. *Valence*, II, IV, VI, and VIII.

History.—The ore called *pyrolusite*, or black oxide of manganese, was known to the early chemists, by whom it was confounded with magnetic oxide of iron or magnetite.

In 1740, Pott showed that this mineral did not contain iron, and, in 1774, Scheele recognized it as very different from the ores of iron, and further investigated it.

The metal was first separated by Gahn, in the same year, and later, in larger quantities, by St. Claire-Deville and Brunner.

The name manganese is supposed to have been given the new element to distinguish it from magnesia.

Occurrence.—Manganese occurs in nature as a frequent associate of iron, to which by its properties it is closely related. It exists free to a small extent in meteoric iron.

The most widely-occurring ores are the oxides, of which the most important is manganese dioxide, or *pyrolusite*, MnO_2. Besides this it is found as sesquioxide, or *braunite*, Mn_2O_3, as hydrated sesquioxide, or *manganite*, $Mn_2O_3 + H_2O$, as manganomanganic oxide, or *hausmannite*, Mn_3O_4, as carbonate, or *manganese-spar*, $MnCO_3$, as sulphide, or *manganese-blende*, MnS, in many silicious minerals, in some mineral waters, and in plant and animal organisms, which derive it from the soil.

Preparation.—The metal cannot be reduced from its oxides by hydrogen, and only by carbon, after having first been heated to a very high temperature. To prepare manganese, the dioxide is heated with carbon and calcined borax to the highest attain-

able heat of a blast-furnace, or a mixture of manganese chloride, fluor-spar, and sodium is brought in small quantities to a red heat in a Hessian crucible, or a concentrated solution of manganous chloride is electrolyzed. To reduce the ores of manganese in such a manner as to obtain the metal in fit condition for alloys, Green and Wahl have lately introduced the use of silicon, which they add in the form of an iron silicide.

Properties.—This element is a very difficultly fusible, very hard, brittle, lustrous metal, which has much the appearance of cast-iron. It has a specific gravity of 7.2. It possesses a very great affinity for oxygen, with which it combines in moist air at ordinary temperatures,—a property which necessitates keeping it under oil or in well-sealed vessels. Cast-manganese containing iron is, however, unalterable in the air. Manganese melts at a white heat, and is weakly magnetic. In fine powder it decomposes water at about 20°. The metal is easily soluble in acids with the liberation of hydrogen.

Uses.—In the pure state it has little use, but as alloys with iron in *spiegeleisen* or ferro-manganese for the production of steel, and with copper and zinc for the preparation of manganese-bronze, it is extensively employed.

Alloys.—These are usually obtained by reducing the manganese and other oxides with coal, or by the process of Green and Wahl mentioned above. Spiegeleisen that contains 25 per cent. and upward of manganese attains a granular structure, and is known as *ferro-manganese.* These materials are used in white cast-iron, the color of which is due to this ingredient. An alloy of manganese, copper, and zinc is known, that closely resembles *German silver. Manganese-bronze* contains 15 parts of copper, 4 parts of manganese, and 1 part of zinc. When these alloys have a manganese content of 3 to 8 per cent. they are soft and ductile, but by 12 or 15 per cent. they are rendered hard and brittle.

MANGANESE AND THE HALOGENS.

Manganous Chloride, $MnCl_2.4H_2O$.—This is obtained as a side product in the preparation of chlorine from manganese dioxide and hydrochloric acid. In the residual liquid it is mixed with iron, from which to separate it the filtered liquid is evaporated to dryness to expel free acid, the residue treated with water, and the resulting solution heated with an excess of manganous carbonate. After filtration the solution is evapo-

rated and allowed to crystallize. The manganous carbonate required for the operation is previously prepared from some of the iron containing liquid by precipitation with sodium carbonate. Should lead and copper be present, they are precipitated by hydrogen sulphide after the iron has been separated and before the solution is concentrated for crystallization. It is a pink, deliquescent salt.

Manganic Chloride, Mn_2Cl_6, and *Manganese Tetrachloride*, $MnCl_4$, have never been isolated, for they readily decompose, giving chlorine and manganous chloride.

Manganous Bromide, $MnBr_2.4H_2O$, and *Manganous Iodide*, $MnI_2.4H_2O$, are pink, deliquescent salts obtained by dissolving manganous carbonate in hydrobromic or hydriodic acid.

MANGANESE AND OXYGEN.

Manganous Oxide, MnO, is obtained as a green powder by heating manganous carbonate, or an oxide of manganese that is richer in oxygen, in a stream of hydrogen. It is a strong base, and dissolves easily in acids with the formation of manganous salts.

Manganous Hydrate, $Mn(OH)_2$.—Manganous oxide forms a hydrate of an unstable character, as a white, flocculent precipitate when a solution of a manganous salt is decomposed by potassium or sodium hydrate. It is insoluble in excess of either precipitant, but is soluble in ammonium hydrate. It soon acquires in the air a brown color, due to partial change to manganic hydrate, which is insoluble in all the alkali hydrates.

Manganese Sesquioxide, Mn_2O_3, occurs in nature as braunite crystallized in brown-black, lustrous, very hard, obtuse quadratic pyramids. It is usually prepared and of the same color by careful ignition of manganous hydrate, manganese dioxide, or manganic nitrate. It is a very weak base, in consequence of which it combines with acids only with difficulty.

Hot hydrochloric acid effects solution with liberation of chlorine and production of manganous chloride.

Manganic Hydrate, $Mn_2(OH)_6$.—As mentioned above, this compound results from the oxidation of manganous hydrate, and is prepared by allowing that change to take place. In cold hydrochloric acid it dissolves to a dark-brown liquid, which is considered to contain manganic chloride, the instability of which is shown by its decomposition into manganous chloride and chlorine when the solution is gently warmed. It is used in the preparation of varnishes.

The mineral manganite has the composition $Mn_2O_3.H_2O$.

Manganoso-manganic Oxide, Mn_3O_4, occurs native as hausmannite in brown-black quadratic pyramids. It results upon the continued ignition of the oxides of manganese, of the hydrates, and of the carbonate with access of air. With evolution of chlorine it dissolves in hydrochloric acid to yield manganous chloride.

Manganese Dioxide, MnO_2. **Mangani Dioxidum**, U. S. P.— This most important of manganese ores was known and used in the Middle Ages. It is often called black oxide of manganese or pyrolusite. The largest deposits are in the Russian Caucasus, Chili, Cuba, Germany, France, and in the United States in Virginia, Arkansas, and Colorado. It crystallizes in steel-gray, more or less lustrous, rhombic masses, which usually enter commerce in a compact or striated state. The dioxide can be artificially prepared by carefully heating manganous oxide with potassium chlorate, or by repeated treatment of manganous oxide with hot concentrated nitric acid, or by moderate heating of the corresponding hydrate.

From the manganous chloride residues left upon making chlorine the manganese is recovered by Weldon's process, which depends upon the formation of dioxide when air is blown through the residue mixed with milk of lime. Upon paper or porcelain it gives a gray-black streak, and when crushed a graphite-colored powder. The other oxides give brown stains and powders. The specific gravity of the mineral varies between 4.7 and 5.1. It is not attacked by water, nitric acid, or dilute sulphuric acid. When heated with strong sulphuric acid to 100° it gives manganic sulphate, while at 200°, manganous sulphate results. In the presence of easily oxidizable organic substances, such as sugar or oxalic acid, it dissolves in dilute sulphuric acid with liberation of oxygen, which acts upon the organic matter present.

Hydrochloric acid yields with the dioxide chlorine and manganous chloride. At a low red heat it gives off one-fourth of its oxygen and changes to sesquioxide, while at a higher temperature it gives up one-third, and passes into manganoso-manganic oxide. The pyrolusite of commerce is not pure, but contains, besides other oxides of manganese, variable quantities of calcium and barium carbonates and sulphates, silica, and iron oxides. The official requirement is the native compound containing at least 66 per cent. of pure dioxide, estimated by the amount of ferrous sulphate that is oxidized when that substance is boiled

with the sample and hydrochloric acid. With some basic oxides manganese dioxide forms salts known as manganites. The acid corresponding to these compounds is not recognized in the free state.

Uses.—Manganese dioxide serves for the preparation of other manganese compounds, of oxygen, of chlorine, and for the decolorization of glass, in which it corrects the green color imparted by the iron oxide derived from the sand used. Aside from the last use, it is employed to give an amethyst color to glass.

Manganic Anhydride, MnO_3, has not yet been prepared, nor is the corresponding hydrate, or manganic acid, H_2MnO_4, known in the free state. The salts of the acid, however, are well known under the name of manganates.

Potassium Manganate, K_2MnO_4.—This compound is made by evaporating 100 parts of potash lye of specific gravity 1.33 in a bright iron kettle to about one-third its weight, and adding to the fused potassium hydrate so obtained 30 parts of manganese dioxide and 28 parts of potassium chlorate, separately powdered and previously mixed on a sheet of paper. The mass is then dried with constant stirring to a stiff consistency, and then heated in a Hessian crucible to a low red heat until a small quantity taken out and put into water almost completely dissolves with an intense green color:

$$3MnO_2 + 6KOH + KClO_3 = 3K_2MnO_4 + KCl + 3H_2O.$$

The heating of the mixture must not be carried to full fusion, or decomposition of the manganate ensues. When the reaction has been shown to be complete, the mass is poured out on an iron plate, and, when cold, is broken and extracted with water. The solution is filtered through asbestos, and then evaporated in a rarefied atmosphere, whereby the salt is obtained in dark-green, almost black crystals.

For technical purposes it is also prepared by melting solid potasssium hydrate with finely-powdered manganese dioxide, with or without the addition of potassium nitrate.

The crystals of this substance are isomorphous with those of potassium sulphate. They dissolve in water to give a dark-green color. When allowed to stand, the color of this solution gradually passes through blue and violet into red, on account of the formation of potassium permanganate. This change is hastened by heat and by the action of carbon dioxide, nitric acid, chlorine, and bromine.

Because of these changes in color the early chemists called the salt *chameleon mineral*, although the same name has also been applied to the permanganate.

Organic substances, sulphur dioxide, and other reducing bodies decolorize a solution of potassium manganate by taking up its oxygen. For this reason its solutions cannot be filtered through paper.

By substituting the corresponding sodium compounds in relative proportion, green crystallized sodium manganate, $Na_2MnO_4 + 10H_2O$, can be obtained by the method employed for the potassium salt.

Barium Manganate, $BaMnO_4$, is easily produced by roasting a mixture of 1 part of powdered manganese dioxide with 4 parts of barium nitrate, and rapidly lixiviating the green mass. It is an emerald-green, crystalline, insoluble powder, sometimes called *barium green*.

Potassium Permanganate, $K_2Mn_2O_8$. **Potassii Permanganas, U. S. P.**—To prepare this salt the green, fused mass obtained in making potassium manganate is treated with twice its weight of hot water. After stirring, the mixture is allowed to settle, and the clear, green solution produced is poured off. The sediment is washed with more water by affusion and decantation after subsidence. The mixed clear solutions are warmed in a water-bath, at which temperature a current of carbon dioxide is conducted into the liquid until a pure red-violet color has been acquired:

$$3K_2MnO_4 + 2CO_2 = K_2Mn_2O_8 + MnO_2 + 2K_2CO_3.$$

The manganate can also be converted into permanganate by thoroughly boiling the solution, potassium hydrate resulting as one of the products of the change:

$$3K_2MnO_4 + 2H_2O = K_2Mn_2O_8 + MnO_2 + 4KOH.$$

In both cases a precipitate of hydrated dioxide is produced.

After standing, the clear solution is siphoned off, and the last turbid portion is filtered through asbestos. Care having been taken to exclude dust, the liquid is evaporated until a pellicle forms on the surface, and then allowed to cool. The crystals which separate are collected and placed to drain out of contact with organic matter. The salt may be obtained in a crude state by evaporating the solution at once to dryness. It forms metallic, lustrous, almost black, rhombic prisms, which are permanent in the air. These are soluble in 16 parts of water at 15°, and in 3

parts of boiling water. The solution gradually undergoes change. Potassium permanganate is a powerful oxidizing agent toward organic and inorganic substances. In neutral solution one molecule of the salt gives up three atoms of oxygen, with the production of a brown, flocculent precipitate of a hydrated dioxide.

In acid solution one molecule gives up five atoms, and if sufficient of the oxidizable matter is present, a clear and colorless solution results. On account of the ease with which they yield their oxygen, both manganate and permanganate are employed as disinfectants: foul-smelling gases or substances are rendered entirely odorless by contact with these compounds. Its use in the quantitative analysis of iron and of organic matter in potable waters depends upon this same feature. Chlorine is liberated by the action of hydrochloric acid on potassium permanganate. The salt is occasionally used in the practice of medicine.

Sodium Permanganate, $Na_2Mn_2O_8.6H_2O$, is prepared by a method similar to that used for making the potassium salt. It is a very hygroscopic, and therefore difficultly crystallizable, substance.

Ammonium Permanganate, $(NH_4)_2Mn_2O_8$, is isomorphous with the potassium compound. It results upon the double decomposition of molecular quantities of barium permanganate and ammonium sulphate, or of silver permanganate and ammonium chloride. It is easily decomposed by heat.

Barium Permanganate, $BaMn_2O_8$, forms needle-shaped, almost black crystals, and is gotten by the action of carbon dioxide on barium manganate suspended in water, or by reacting on silver permanganate with barium chloride.

Zinc Permanganate, $ZnMn_2O_8$, as easily-decomposable, deep dark-red, lustrous crystals, is prepared by decomposition of barium permanganate by the proper amount of zinc sulphate, or of silver permanganate by zinc chloride, and evaporation of the supernatant liquid *in vacuo*.

Permanganic Acid, $H_2Mn_2O_8$, is known only in aqueous solution. It may be made by the action of dilute sulphuric acid on barium permanganate, or by boiling a manganese compound that is free from chlorine with nitric acid in the presence of red oxide of lead. The production of its rose-red color by the last method is used as a test for manganese under the name of Crum's process.

Permanganic Anhydride, Mn_2O_7, is the oxide which corresponds to permanganic acid. As a heavy, greenish-black, readily decomposing liquid, it is produced when potassium permanga-

nate is added in small quantity to well-cooled concentrated sulphuric acid.

The greatest care should be exercised in the application of these substances as oxidizing agents, as explosion is likely to occur if the action is sudden.

MANGANESE AND SULPHUR.

Two sulphides of manganese are found native. Manganese monosulphide, MnS, occurs as *manganese-blende* in black, cubic crystals, and manganese disulphide, MnS_2, as *hauerite* in red-brown crystals of the same system.

The former sulphide may be prepared as a green powder by heating manganese sesquioxide in a stream of hydrogen sulphide, or by precipitating a solution of a manganous salt with an alkali sulphide, whereby a flesh-pink precipitate of a hydrated sulphide is thrown down. Upon exposure to air, this takes up oxygen and assumes a brown color.

OXYGEN SALTS OF MANGANESE.

Manganous Sulphate, $MnSO_4.4H_2O$. **Mangani Sulphas, U. S. P.**—This salt is prepared by rubbing a convenient quantity of finely-powdered dioxide of good quality to a thick paste with concentrated sulphuric acid, then heating the mixture in a Hessian crucible by a blast-furnace gradually to low redness, and maintaining that condition as long as white fumes of sulphur trioxide are evolved :

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$

From time to time a portion of the mass is taken out, allowed to cool, and treated with water. The solution is then filtered and tested for iron, which, if found, necessitates heating the materials to full redness, until after another trial the water solution is found to be destitute, or nearly so, of iron.

The gray-white mass is allowed to cool, and is then powdered and extracted with three times its weight of hot water, which, by frequent stirring, dissolves the salt.

Most, if not all, of the iron is left undissolved as oxide. Any traces remaining in solution are removed by manganous carbonate, which precipitates the impurity as hydrate. The filtered, iron-free solution is slowly evaporated at a low temperature.

Lead and copper are removed by saturating the liquid with hydrogen sulphide previous to evaporation, while zinc is sepa-

rated by the same reagent, but in the presence of sodium acetate and acetic acid.

Manganese sulphate forms pale, rose-colored crystals which are somewhat efflorescent, and the amount of whose water of crystallization and whose crystalline form vary according to the temperature at which the crystals separate. Besides that of official composition which contains four molecules of water of crystallization, and which is obtained in rhombic prisms between 20° and 30°, monoclinic crystals having the formula $MnSO_4.7H_2O$ can be produced below 6°. They are isomorphous with ferrous sulphate. Between 7° and 20° a salt of the composition $MnSO_4.5H_2O$ crystallizes in the triclinic system, which also includes copper sulphate. When the solution is evaporated at a temperature above 30°, an almost colorless, difficultly soluble, crystalline powder of still lower percentage of water separates.

The official salt is soluble in an equal weight of water to produce a neutral solution. It is not soluble in alcohol. With the sulphates of potassium and sodium, it gives double salts. Manganous sulphate finds a limited use in medicine.

Manganic Sulphate, $Mn_2(SO_4)_3$, is a dark-green, deliquescent powder which results from the action of concentrated sulphuric acid on manganese sesquioxide or on the dioxide at from 100° to 140°.

Manganese alums crystallize in octohedra, and arise from the union of the alkali sulphates with manganic sulphate.

Manganous Nitrate, $Mn(NO_3)_2.6H_2O$, separates in deliquescent crystals when manganese carbonate is added to nitric acid and the solution is evaporated.

Manganous Phosphate, $Mn_3(PO_4)_2.7H_2O$, is produced as a white precipitate by the addition of sodium phosphate to a solution of manganous sulphate.

Manganese Borate is formed when a solution of a manganous salt is precipitated by sodium borate. The white precipitate thrown down becomes brownish upon drying.

Manganous Carbonate, $MnCO_3$.—Manganese-spar, the native form of this compound, occurs in red, hexagonal crystals, which are contaminated with iron and other carbonates. The artificial white salt is prepared by adding a slight excess of sodium carbonate to a solution of manganous sulphate. Upon drying it undergoes some decomposition and becomes darker on account of the sesquioxide formed. When ignited it loses carbon dioxide and leaves manganoso-manganic oxide.

MOLYBDENUM, TUNGSTEN, URANIUM.

In addition to chromium and manganese, in the foregoing group we have the rarer elements molybdenum, tungsten, and uranium.

The whole group possesses many points of resemblance to the sulphur group of non-metals. The members have an equivalence II, IV, VI, and some of them more rarely VIII.

Molybdenum, Mo. *Atomic Weight*, 95.9.—This element occurs in nature chiefly as *molybdenite*, MoS_2, and as *wulfenite*, a lead molybdate, $PbMoO_4$. It is more rarely found as the trioxide, MoO_3.

Molybdenum is prepared by heating the chloride or oxide to a high temperature in a current of hydrogen. It is a silver-white, infusible metal, harder than topaz, and having a specific gravity of 8.6. It is permanent in the air, unless heated, when it is slowly converted into the trioxide. Hydrochloric, hydrofluoric, and dilute sulphuric acids do not dissolve it, but it is readily attacked by nitric acid and nitro-hydrochloric acid.

Molybdenum Trioxide, MoO_3, is the final product of the oxidation of the metal. The other oxides are prepared from this by various processes of reduction. They are MoO_2, Mo_2O_3, and MoO.

Molybdic Acid is a term applied to the trioxide, and its combinations with various bases are known as molybdates.

Ammonium Molybdate, $(NH_4)_2MoO_4$, is formed by dissolving molybdenum trioxide in solution of ammonia, and precipitating the salt formed by the addition of alcohol.

Phosphomolybdic Acid is prepared by the union of phosphoric and molybdic acids.

The one richest in molybdenum, obtained by evaporating an aqueous solution of these two acids, has the composition $2H_3PO_4, 24MoO_3.58H_2O$. It occurs in yellow crystals, and loses water at 140°.

Ammonium Phosphomolybdate, $12(MoO_3),(NH_4)_3PO_4.2H_2O$, is the compound which is formed when ammonium molybdate in the presence of nitric acid is added to phosphoric acid or a phosphate.

Tungsten (Wolfram), W, *Atomic Weight*, 183.6, is found in nature as *wolframite*, an iron and manganese tungstate. Like molybdenum, it forms a great number of compounds, and as *tungstic acid* combines with bases to form a great variety of salts.

Uranium, U, *Atomic Weight*, 238.8, occurs in nature chiefly as the mineral *uranite*, or *pitch-blende*, U_3O_8. It has many characters in common with molybdenum and tungsten, but possesses more basic properties. The metal is not so permanent, and ignites when heated with access of air to 170°. It has a specific gravity of 18.4.

Three chlorides of uranium are known, as follows: the *trichloride*, UCl_3, the *tetrachloride*, UCl_4, and the *pentachloride*, UCl_5.

The *dioxide*, UO_2, and the *trioxide*, UO_3, are known; the latter is basic towards acids, and forms salts containing the bivalent radical *uranyl*, UO_2. The uranyl salts are yellow, and impart to glass when fused with it a remarkable fluorescence.

CHAPTER X.

THE IRON GROUP.

THIS group includes iron, nickel, and cobalt. In the periodic system they form a transition group between manganese and copper. They are distinguished, moreover, from the other metals by their magnetic properties.

IRON.

Symbol, Fe. *Atomic Weight*, 55.88. *Valence*, II, IV, $(Fe_2)^{VI}$ and VI.

History.—The discovery of iron antedates the earliest historical times, as it was known to the ancient Egyptians and Assyrians, and is mentioned in the Pentateuch. The earliest form was undoubtedly malleable iron, prepared direct from the ore by smelting with charcoal, as is still carried out in a primitive way in India. Steel was also known to the ancient Greeks, and is described by Homer, the Chalybes, a tribe on the coast of the Black Sea, being famed for its production. The manufacture of cast-iron by the blast-furnace process appears to date from the end of the fifteenth century.

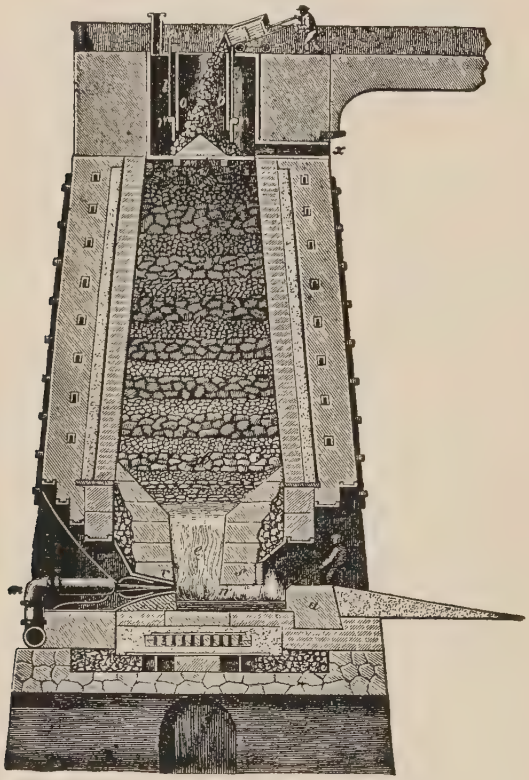
Occurrence.—Iron occurs as *native metal*, but not certainly of terrestrial origin; on the other hand, meteoric iron is frequently found. These meteorites, which fall upon the earth, coming from an unknown source, may be largely made up of mineral matter, or they may contain as much as 93 per cent. of metallic iron, always associated with metallic nickel, and occasionally small quantities of other metals. Iron also occurs as ferric oxide under the name of *hematite* (or specular iron), as ferroso-ferric oxide under the name of *magnetite*, as hydrated ferric oxide under the name of *limonite* (or brown hematite), and as carbonate under the name of *siderite* (spathic iron). The ferric sulphide, which occurs so abundantly under the name of *pyrite*, is not used as an ore of iron, although valuable for the manufacture of sulphuric acid. Other valuable iron minerals are *vivianite*, or the phosphate (found in green marl), *arseno-pyrite*, or the sulpharsenite, and *wolfram*, or the tungstate of iron.

Preparation.—Iron is manufactured on a large scale in three

commercial varieties, differing in both physical and chemical characters,—viz., cast-iron, wrought-iron, and steel. According to the present method of working the ores, cast-iron is the first variety obtained.

Cast-iron.—While the earliest processes for the manufacture of iron allowed of the production of a relatively pure iron direct from the ore, such production was wasteful and expensive. The

FIG. 141.



Sectional view of blast-furnace.

ore is now first submitted to the blast-furnace treatment, and the product is an iron containing from 3 to 6 per cent. of carbon, together with smaller amounts of other elements, such as silicon and phosphorus, and, it may be, manganese. The theory of the blast-furnace may be readily understood from Fig. 141. A tall, cylindrical or conical chamber, lined with fire-brick, is filled with

fuel, ore, and flux (limestone) in certain proportions, the three materials being stratified as shown. At the base a blast of hot air is blown in. This forms carbon monoxide with the fuel, and this reducing gas meeting the layer of highly-heated ferric oxide (ore) reduces it to metal, carbon dioxide being formed. This, in turn, meeting the next layer of heated fuel is changed to monoxide, which again acts as a reducing agent. The lime of the limestone takes up the silica and alumina of the impurities and forms with them a fusible slag. The molten iron, however, has the power of dissolving carbon, part of which it retains as a carbide of iron, and part separates in scales as graphite. The iron settles to the bottom of the furnace because of its higher gravity, while the lighter slag remains floating upon its surface, and is periodically drawn off at a somewhat higher level than the opening through which the molten iron is run. *White cast-iron* contains the whole of its carbon in the combined state, while *gray cast-iron* contains much of the carbon uncombined as graphite, and *mottled iron* is of intermediate character.

Spiegeleisen is a white cast-iron of very crystalline character, and containing manganese as an essential constituent.

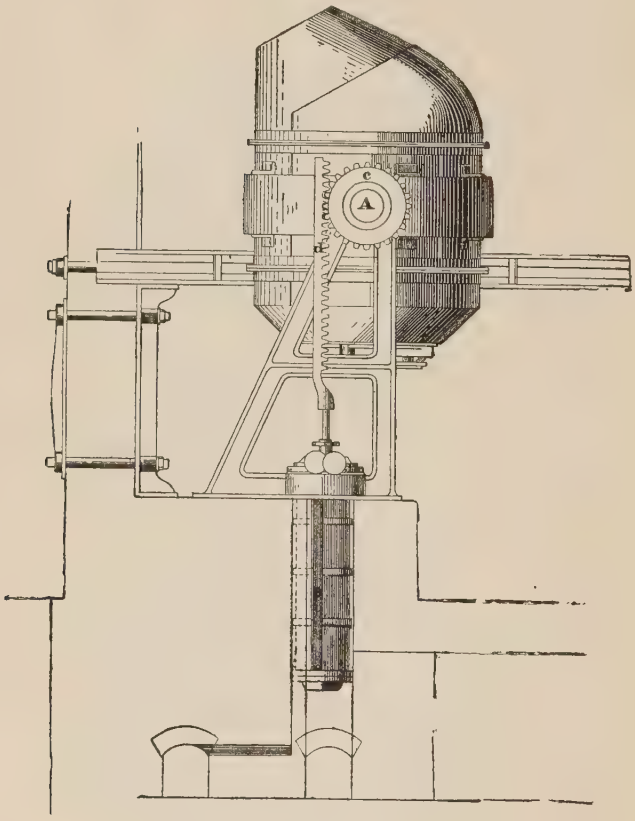
Cast-iron has a crystalline, granular structure on a fractured surface, is very hard and brittle, and melts at from 1150° to 1200°. Its specific gravity is about 7.1.

Wrought-iron.—This is the purest variety of manufactured iron. It contains less than 0.5 per cent. of carbon, and is nearly free from the impurities of silicon and phosphorus contained in the cast-iron. It is made from this latter mainly by what is termed the "puddling process." This consists in melting cast-iron on the hearth of a reverberatory furnace along with a layer or "felting" of ferric oxide, and working together of the mixture while exposed to the oxidizing flame. The carbon and silicon of the cast-iron are oxidized, the former burning off as gas, and the latter forming the "tap-cinder" or slag. The phosphorus and sulphur are also carried off in this slag. As the iron becomes pure it becomes pasty, and the "blooms" or masses of agglutinated mixture are squeezed and hammered to get rid of the slag and to weld the porous iron together into a fibrous and homogeneous mass. The wrought-iron so obtained has a specific gravity of 7.6 to 7.8, is soft and tough, and at a red heat may be forged, rolled, and welded. It fuses at about 1500°.

Steel in chemical composition stands intermediate between cast-iron and wrought-iron, and may be made from either as the start-

ing-point. The first method, and for a time the only one, was the "cementation process." In this the bars of wrought-iron cut in short lengths are packed with fine charcoal in fire-clay chests or "troughs," and heated to about 1100° for from 4 to 8 days, when the bars are found to be converted into hard steel, known as *blister steel.* This is then frequently melted in plum-

FIG. 142.



Bessemer converter.

bago crucibles at a white heat and cast into ingots known as *crucible steel,* which is the hardest and finest variety, and is used for edged tools and temper steel. The second method of steel-making is the Bessemer process, which, as has well been said, is the greatest metallurgical discovery that has ever been made. In this we start with cast-iron, of which some 4 to 10 tons are melted

in one charge in a vessel known as the "converter," and a powerful blast of air is blown through the molten metal until the necessary amount of carbon has been burned out. The Bessemer converter is shown in Fig. 142 in general view. The converter, which is lined with fire-brick, is first heated to a bright red heat and put into a horizontal position. The pig-iron is then run in from a cupola, or it may be direct from the blast-furnace, and the blast turned on when the converter is swung back into a vertical position. The reaction lasts some 20 minutes, and is known to be complete by the change in the appearance of the flame that issues from the mouth of the converter. In this time the carbon of the cast-iron is almost entirely burned out, leaving what might be called a wrought-iron. The converter is, therefore, returned to the horizontal position, the blast is shut off, and a certain quantity (some 7 per cent.) of spiegel-iron, rich in carbon and manganese, is added to the charge, which gives to the iron the quantity of carbon necessary for its transformation into steel, while the manganese reduces what oxide of iron has formed in the molten mass. The presence of phosphorus in more than the most minute quantity is very injurious to the quality of steel, and in making steel by the original Bessemer process it was necessary to select pig-iron containing the least of this element. A modification of the process was therefore made in order to enable good steel to be made from pig-iron containing larger quantities of phosphorus. This modification is known as the *basic* Bessemer process, and consists in lining the converter with a mixture of lime and magnesia, obtained by calcining dolomite. These bases absorb the phosphorus with the production of phosphates of calcium and magnesium, and, after use, the so-called basic brick containing these substances are sold to the fertilizer industry. The third process for the manufacture of steel is the "open-hearth" or Siemens-Martin process. In this is taken either a mixture of pig-iron and ore, which is heated with a reverberatory flame, as in the puddling process, or bars and blooms of wrought-iron are heated with the pig-iron, and steel is made by the combination of the two. The steel so obtained is run, while in the molten state, through suitable channels into ingot moulds to solidify.

Steel contains 0.8 to 1.5 per cent. of carbon, all of which is chemically combined with the iron. Its specific gravity is 7.6–8.0. It has a fine-grained structure, and melts at about 1400°. If cooled rapidly it becomes hard and brittle ; if cooled slowly it is

soft, and may be forged and welded. Steel is tempered by reheating it to temperatures varying from 220° to 320°, according to the use intended, and then allowing it to cool slowly. It thus acquires elasticity combined with hardness.

The production of pig-iron in the United States in 1896 was 8,623,127 tons, and in 1897, 9,491,976 tons, while in Great Britain the output for the same years was 8,659,681 tons and 8,850,000 tons respectively. The steel production of the United States was for 1896, 5,582,606 tons, and for 1897, 6,500,000 tons.

Properties.—The purest of the commercial varieties just mentioned is wrought-iron. Accordingly this is taken as the official iron of the Pharmacopœia (**Ferrum,** U. S. P.), and is described as "metallic iron in the form of fine bright and non-elastic wire." Its other characters have been given under wrought-iron. Another form of the metal recognized officially is *reduced iron* (**Ferrum Reductum,** U. S. P.). This is iron reduced from the sesquioxide by hydrogen. The oxide is directed to be prepared by the U. S. Pharmacopœia of 1870 by calcining the thoroughly-washed subcarbonate. The reduced iron forms an iron-gray powder without metallic lustre, readily oxidizing on exposure to air, and liable to contain some oxide of iron from imperfect reduction or after oxidation.

COMPOUNDS OF IRON.

Iron forms two well-defined series of compounds : the *ferrous*, in which it has the valence II, and the *ferric*, in which we have the group Fe_2, with the valence VI. Of these the latter class are the more stable. There is also a ferric acid in which the metal acts with the valence VI, and plays an electro-negative or acid-forming part.

IRON AND THE HALOGENS.

Ferrous Chloride, $FeCl_2$, may be obtained crystallized from hydrochloric acid solutions in green monoclinic prisms which are deliquescent. An anhydrous salt is also obtained by passing hydrochloric acid over heated iron, and sublimes in white leaflets.

Ferric Chloride, Fe_2Cl_6. **Ferri Chloridum,** U. S. P.—The official salt crystallizes with $12H_2O$ indistinctly in orange-yellow masses, which are "inodorous and of a strongly chalybeate and styptic taste and an acid reaction. It is very deliquescent in moist air. Very soluble in water and alcohol. It melts at 35.5°,

forming a reddish-brown liquid." When strongly heated it is decomposed, hydrochloric acid fumes escaping, and a mixture of chloride and oxide remaining. An aqueous solution of ferric chloride is official (**Liquor Ferri Chloridi,** U. S. P.), "containing about 37.8 per cent. of the anhydrous salt, corresponding to 62.9 per cent. of the crystallized salt." It is also official as tincture (**Tinctura Ferri Chloridi,** U. S. P.).

Ferrous Bromide, $FeBr_2$, may be obtained crystallized with $6H_2O$ in bluish-green, rhombic tablets, or anhydrous as a yellowish crystalline mass.

Ferric Bromide, Fe_2Br_6, may be obtained in the form of dark-red crystals by heating iron in an excess of bromine vapor. It is deliquescent, and its solution dissolves ferric hydrate readily with formation of soluble oxybromides.

Ferrous Iodide, FeI_2, is readily obtained in nearly colorless solution by warming a mixture of iodine and iron filings with water. This solution readily oxidizes on exposure to the air with separation of iodine. It is therefore protected from oxidation by being admixed with sugar of milk and then evaporated down, reduced to powder, and kept in a well-stoppered bottle. The product is the official saccharated ferrous iodide (**Ferri Iodidum Saccharatum,** U. S. P.).

Ferric Iodide, Fe_2I_6, may be prepared by heating iron filings with an excess of iodine, but is unstable, and decomposes on cooling into ferrous iodide and free iodine.

Both *Ferrous Fluoride*, FeF_2, and *Ferric Fluoride*, Fe_2F_6, have been obtained, and are relatively stable. The former may be had crystallized with 8 molecules of H_2O in greenish prisms, and the latter in colorless crystals with 9 molecules of H_2O.

IRON AND OXYGEN.

Ferrous Oxide, FeO, is obtained as a black powder either by reducing ferric oxide with carbon monoxide or by heating ferric oxide to 300° and passing hydrogen over it. It readily oxidizes, and when prepared by this latter method becomes incandescent on exposure to the air, so rapid is the oxidation.

Ferrous Hydrate, $Fe(OH)_2$, is thrown out of ferrous solutions by the alkalies as a greenish-white precipitate. It soon absorbs oxygen, and changes first to a dirty green and then to a reddish brown. Ferrous hydrate is also formed by the action of pure water containing air in solution on iron. It dissolves in about 150,000 parts of water with an alkaline reaction.

Ferric Oxide, Fe_2O_3, is found abundantly in nature as red

hematite or specular iron. Artificially it is prepared by igniting the hydrate or any ferric salt containing a volatile acid, forming what looks at first like a steel-gray powder, but which, when finely ground, takes a brownish-red color. It is also obtained on a large scale, when fuming sulphuric (or Nordhausen) acid is distilled from green vitriol, as a dark-red powder under the name of "colcothar" or *caput mortuum*, and is used as polishing-powder and as a basis of paints. Natural ochres also furnish an oxide which, after ignition, proves valuable for use as a pigment.

Ferric Hydrate, $Fe_2(OH)_6$ (**Ferri Oxidum Hydratum**, U. S. P.), is formed when a ferric solution is precipitated by adding an excess of ammonia. It appears as "a brownish-red magma, wholly soluble in hydrochloric acid without effervescence." On boiling it becomes more compact, gives up water, and is converted into the hydrate $Fe_2O(OH)_4$ (or $Fe_2O_3 + 2H_2O$). The same change takes place gradually by the prolonged contact of the precipitated hydrate with water, and ultimately a bright-red amorphous powder of the composition $Fe_2O_2(OH)_2$ (or $Fe_2O_3 + H_2O$) remains. Neither of these lower hydrates is as efficient an arsenic antidote as the freshly-precipitated ferric hydrate. Freshly-precipitated ferric hydrate is soluble in solution of ferric chloride with dark-red color owing to the formation of a basic chloride. If this solution be allowed to dialyze we can obtain a liquid containing 98.5 per cent. of ferric hydrate and 1.5 per cent. of hydrochloric acid. These solutions are known as "Dialyzed Iron."

Ferroso-ferric Oxide, Fe_3O_4 (or $FeO.Fe_2O_3$).—This combination of the two oxides of iron is found abundantly in nature as the magnetic or black oxide of iron. It is also formed when iron is quickly burned in oxygen or when steam is passed over ignited iron. The iron scale that forms when wrought-iron is heated in the air is a varying mixture of ferrous and ferric oxides.

Similar combinations of ferric oxide with other protoxides occur in nature as the mineral *Franklinite* (containing zinc oxide with ferric oxide), while in *Chromite* (or chromic iron) we find chromium sesquioxide with ferrous oxide in combination.

Ferric Acid.—When iron filings are fused with nitre we obtain a cherry-red fused mass from which water dissolves out *potassium ferrate*, K_2FeO_4. This compound may be obtained in crystals isomorphous with potassium chromate and sulphate. It is, however, unstable and soon decomposes. The free acid, H_2FeO_4, has not been obtained.

OXYGEN SALTS OF IRON.

Ferrous Sulphate, $FeSO_4.7H_2O$ (**Ferri Sulphas**, U. S. P.), has long been known under the name of *green vitriol*. It forms "large, pale bluish-green, monoclinic crystals, without odor, and with a saline, styptic taste; efflorescent in dry air." In moist air, the crystals rapidly absorb oxygen and become coated with a brownish-yellow crust of basic ferric sulphate. It is readily soluble in water, insoluble in alcohol. The aqueous solution of the salt has an acid reaction. When heated the salt loses 6 molecules of water at 100° and the seventh only at 300°. The official dried ferrous sulphate (**Ferri Sulphas Exsiccatus**, U. S. P.) is stated to have approximately the composition $2FeSO_4.3H_2O$, and forms a grayish-white powder. The official granulated salt (**Ferri Sulphas Granulatus**, U. S. P.) has the same composition, $FeSO_4.7H_2O$, as the crystals, but is got in crystalline powder by allowing the clear aqueous solution to run into alcohol, in which the salt is insoluble.

Ferrous sulphate forms crystallizable double salts with alkali sulphates, as $FeSO_4,(NH_4)_2SO_4.6H_2O$. As these double salts are more stable than the ferrous sulphate by itself and oxidize only slowly in the air, they are often used in the laboratory.

Ferric Sulphate, $Fe_2(SO_4)_3$, forms a white mass which gradually dissolves in water with a reddish-brown color. The solution is official as **Liquor Ferri Tersulphatis**, U. S. P. Ferric sulphate unites with alkali sulphates to form iron alums. Of these, the ammonium alum, $Fe_2(SO_4)_3(NH_4)_2SO_4.24H_2O$, is official as **Ferri et Ammonii Sulphas**, U. S. P. It crystallizes in "pale violet, octohedral crystals, without odor, and having an acid, styptic taste; efflorescent on exposure to the air." It is soluble in water, insoluble in alcohol.

A basic or subsulphate of iron is also official in solution as **Liquor Ferri Subsulphatis**, U. S. P., known commonly as *Monsel's Solution*. In its preparation, the ferrous sulphate taken is converted into ferric sulphate at the expense of the nitric acid added; but the sulphuric acid mixed with the nitric is in quantity insufficient to form the normal salt. The formula assigned to the salt contained in this solution is $Fe_4O(SO_4)_5$, or according to other authorities $Fe_2(SO_4)_3 5Fe_2O_3.H_2O$.

Ferric Nitrate, $Fe_2(NO_3)_6$, is formed when iron is dissolved in nitric acid. It crystallizes either with 12 molecules of water in cubes or with

18 molecules in monoclinic crystals, both forms being colorless and deliquescent. A solution of the ferric nitrate is official as **Liquor Ferri Nitratis**, U. S. P.

Ferrous Phosphate, $Fe_3(PO_4)_2.8H_2O$, occurs as the mineral *vivianite* in bluish monoclinic prisms. Obtained artificially it is a white, amorphous powder, which speedily oxidizes in the air.

Ferric Phosphate, $Fe_2(PO_4)_2$, is obtained as a white precipitate on adding sodium phosphate to ferric solutions. It is present in the official scale preparation **Ferri Phosphas Solubilis**, U. S. P.

Ferric Pyrophosphate, $Fe_4(P_2O_7)_3$, is the salt present in **Ferri Pyrophosphas Solubilis**, U. S. P., another scale preparation.

Ferric Hypophosphite, $Fe_2(PH_2O_2)_6$, **Ferri Hypophosphis**, U. S. P., forms "a white or grayish-white powder, odorless and nearly tasteless; permanent in the air." Like other hypophosphites it is readily oxidized by oxidizing agents.

Ferrous Carbonate, $FeCO_3$, occurs in nature as the mineral *siderite* or *spathic iron*. It is artificially obtained by adding sodium carbonate to ferrous solutions, forming a white precipitate which rapidly oxidizes in the air to ferric hydrate. The official preparation **Ferri Carbonas Saccharatus**, U. S. P., protects the carbonate by admixture with sugar. Ferrous carbonate is slightly soluble in water containing dissolved carbon dioxide, and hence is present in the natural chalybeate mineral waters.

Potassium Ferrocyanide and *Ferricyanide* are described later under the cyanogen compounds in Part IV.

The organic salts of iron, such as the Tartrate and Citrate, etc., are also noted in Part IV.

IRON AND SULPHUR.

Ferrous Sulphide, FeS, is obtained artificially by fusing together iron and sulphur. It forms a dark-gray or black metallic mass, which finds extended use in the chemical laboratory as a source of hydrogen sulphide gas. If flowers of sulphur and finely-divided iron are intimately mixed and then moistened with water, the union takes place at ordinary temperatures. Ferrous sulphide is also precipitated as a black precipitate by the use of alkali sulphides, in ferrous solutions directly and in ferric solutions after previous reduction of the iron salt to the ferrous state.

Ferric Sulphide, FeS_2, occurs abundantly in nature as *pyrites*, a mineral used on a large scale in the manufacture of sulphuric acid and green vitriol.

NICKEL.

Symbol, Ni. *Atomic Weight*, 58.6. *Valence*, II and $(Ni_2)^{VI}$.

History.—The ore known as copper-nickel (niccolite) was known as early as 1694 to resemble copper in appearance without containing that metal, but it was only in 1751 that Cronstedt stated that it contained a foreign element to which, in 1754, he proposed to give the name of nickel.

Occurrence.—The most important sources of nickel at present are the mines of New Caledonia, an island in the South Pacific belonging to France, and Sudbury, Ontario ; the most important mine in the United States, that of Lancaster Gap, Pennsylvania, is now nearly exhausted. The ore worked in New Caledonia is the hydrated silicate of nickel and magnesia known as *garnierite* (or *genthite*), while that of Canada and Lancaster Gap is a *nickeliferous pyrrhotite* (magnetic pyrites). The sulphide known as *millerite*, and the arsenide (*niccolite* or copper-nickel), are also well-known ores. The nickel ores, especially the sulphide and arsenide, are always associated with the corresponding cobalt ores.

The production of nickel throughout the world in 1896 was as follows :

New Caledonia	2972 tons.
Canada	1541 "
All other localities	90 "
Total	4603 "

Most of the Canadian ore, however, is smelted and reduced to metal in the United States.

Preparation and Properties.—Such nickel ores as contain sulphur or arsenic are first roasted, and the product, known as "speiss," is then dissolved in hydrochloric acid, and the separation of nickel from the accompanying metals accomplished in the wet way. The New Caledonian ore, being free from arsenic, sulphur, and cobalt, is smelted in a blast-furnace very much like iron ores, or it may be at once treated with hydrochloric acid, and the solution of nickel salt then precipitated with oxalic acid and the oxalate reduced to metal with lime and carbon.

Nickel is a lustrous white metal with a steel-gray tinge. Its specific gravity is 8.9. When pure it is malleable, and can be welded. The cast-nickel formerly obtained from arsenide and sulphide ores did not possess these properties, owing to the combined carbon, which made it like cast-iron. In 1879, Fleitmann

discovered that the addition of ⅛ of 1 per cent. of magnesium rendered the nickel malleable and more fusible. Since then it has been found that manganese in amount from 2 to 5 per cent. would accomplish the same result. The purest nickel has been made by Mond, who takes up the metal in a gaseous compound by passing carbon monoxide over it at a moderate heat, and then at a higher temperature decomposes the compound, separating pure metallic nickel.

Uses of the Metal.—Nickel has long been used in admixture with copper and zinc in the manufacture of German silver; it has also been used with copper alone in coinage alloys, and within the last few years in the manufacture of nickel-steel armor-plate, which has produced a great increase in the demand for the metal. Nickel-plating has also been an important utilization of the metal, as the coating, if well deposited, undergoes scarcely any oxidation, and takes a high polish. The solution from which the plating is done is always that of the nickel-ammonium sulphate.

Nickel Compounds.—Nickel, like iron, forms two well-defined series of salts: the *nickelous* compounds, in which it has the valence two, and the *nickelic*, in which the double atom Ni_2 acts as a hexad group. The former series appear to be the more stable.

Nickelous Chloride, $NiCl_2.6H_2O$, forms green monoclinic prisms, soluble in water and alcohol. When heated they lose water, and when anhydrous show a yellow color.

Nickelous Cyanide, $Ni(CN)_2$, is an apple-green precipitate easily soluble in excess of potassium cyanide, with the formation of a crystalline double salt, $Ni(CN)_2.2KCN$. This salt is easily decomposed by dilute acids, and therefore is not analogous to the ferrocyanides and cobalticyanides.

Nickelous Oxide, NiO, occurs sparingly in nature as the mineral *bunsenite*, and may be obtained artificially by igniting the hydrate, carbonate, or nitrate. It forms a green, crystalline powder.

Nickelous Hydrate, $Ni(OH)_2$, is thrown down, when alkalies are added to nickelous solutions, as a bright-green precipitate. It dissolves in ammonia water with a blue color, and separates out as a green, crystalline powder on boiling the ammoniacal solution.

Nickelous Sulphate, $NiSO_4.7H_2O$.—This salt crystallizes from aqueous solutions in green, rhombic crystals, isomorphous with magnesium sulphate. From solutions containing an excess of acid there separate at ordinary temperatures $NiSO_4.6H_2O$, in bluish-green, quadratic pyramids, and at 50°–70° green, monoclinic crystals of the same composition. The double sulphate used for nickel-plating is $NiSO_4.(NH_4)_2SO_4.6H_2O$.

Nickelous Sulphide, NiS.—The sulphide is found in nature as *millerite*, of brass-yellow color. Obtained by precipitation by alkali sulphides in nickelous solutions it is black.

Nickelic Oxide, Ni_2O_3, is a black powder obtained by gentle ignition of the nitrate or carbonate in air. It behaves like a peroxide, as it dissolves in sulphuric or nitric acid with evolution of oxygen, and in hydrochloric acid with evolution of chlorine.

Nickelic Hydrate, $Ni_2(OH)_6$.—If chlorine be passed through the nickelous hydrate suspended in water, this higher compound is obtained. It is also formed as a black precipitate when the solution of a nickelous salt is warmed with an alkaline hypochlorite.

COBALT.

Symbol, Co. *Atomic Weight*, 58.6. *Valence*, II and $(Co_2)^{VI}$.

History.—Certain ores containing cobalt were known to impart a blue color to glass when smelted with it, and in these Brandt, in 1735, pointed out the presence of a peculiar metal to which he gave the name of *kobalt-rex*. Thus the discovery of cobalt as a distinct element antedates that of nickel.

Occurrence.—Cobalt is found as sulphide (*linnæite*), and as mixed arsenide and sulpharsenide with nickel (*speiss-cobalt* and *cobalt-glance*), and arsenate (*cobalt-bloom*). The New Caledonian mines also afford an ore containing some 3 per cent. of cobaltic oxide, which is smelted by the Maletra Works at Rouen, France.

Preparation and Properties of the Metal.—The arsenical ores of cobalt are roasted and then smelted with limestone or sand, whereby the impurities form a slag, leaving the "cobalt-speiss," which is then dissolved in hydrochloric acid, as in the case of the nickel ores. The final separation of the cobalt from the accompanying metals is effected by the use of bleaching-powder, which precipitates the cobaltic hydrate.

Cobalt is a slightly reddish-white metal, harder than iron, and of specific gravity 8.5–8.7. It is attracted by magnets, but in a lesser degree than iron. It is slowly attacked by sulphuric and hydrochloric acids, more readily by nitric acid. Cobalt is somewhat used for plating upon other metals, like nickel, but most of it is made into the oxide for use in the manufacture of the pigment *smalt*. The total annual production of cobalt is about 200 tons.

Compounds of Cobalt.—Two well-defined series of compounds are formed here also: the *cobaltous* and the *cobaltic*, corresponding to the ferrous and the ferric. The former of these possess a reddish color when in the hydrated state, but become blue when made anhydrous.

Cobaltous Chloride, $CoCl_2$, is obtained by the solution of cobaltous oxide in hydrochloric acid. It forms red, prismatic crystals which dissolve, yielding a pale pinkish solution. This is well known as the basis of

"sympathetic inks;" these leave upon paper almost invisible characters, which when sharply dried become blue.

Cobaltous Oxide, CoO, is obtained as a green powder on heating out of contact with air the cobaltous hydrate.

Cobaltous Hydrate, $Co(OH)_2$, is obtained as a rose-red precipitate on the addition of alkalies to hot cobaltous solutions. In cold solutions a blue basic salt is precipitated.

Cobaltous-Cobaltic Oxide, Co_3O_4, is a compound corresponding to the magnetic oxide of iron, and is obtained when either of the other oxides of cobalt or the nitrate is heated in the air. It forms a black powder.

Cobaltic Oxide, Co_2O_3, corresponding to ferric oxide, is obtained as a dark-brown powder by gently igniting the nitrate.

Cobaltic Hydrate, $Co_2(OH)_6$, is obtained as a brownish-black precipitate if an alkaline hypochlorite is added to a cobaltous solution. This is dissolved by sulphuric acid with liberation of oxygen, and by warm hydrochloric acid with liberation of chlorine; cold dilute hydrochloric acid, however, dissolves it with scarcely any evolution of gas, forming Co_2Cl_6, which decomposes on heating, however, into cobaltous chloride and chlorine.

Cobaltous Sulphate, $CoSO_4.7H_2O$, forms dark-red, monoclinic prisms.

Cobaltous Nitrate, $Co(NO_3)_2.6H_2O$, forms red, deliquescent prisms.

Cobalt Silicates.—When glass of any variety is fused with a cobalt salt a dark-blue color is obtained. This colored glass, when reduced to a powder, is used as a pigment under the name of *smalt*. The application of ores of cobalt for this purpose appears to date from the sixteenth century. Commercial smalt, made from sand, potashes, and roasted cobalt ores, contains usually from 6 to 16 per cent. of cobalt.

Two other pigments are also obtained from cobalt oxide: *Thenard's blue* (or cobalt ultramarine), by igniting it with alumina, and *Rinmann's green*, by igniting it with zinc oxide.

CHAPTER XI.

THE PLATINUM GROUP.

PLATINUM.

Symbol, Pt. *Atomic Weight*, 194.3. *Valence*, II and IV.

History.—There is some evidence that platinum was known to Scaliger, who died in 1558, but not until after 1735—at which time Ulloa carried it to Europe from South America—did this metal begin to receive due attention. Later, Wood, Von Scheffer, and many other prominent chemists studied the element. In 1772, Graf von Sickingen proposed platinum foil and wire for use in chemical analysis, while to Hare, and to Deville and Debray, is due the credit of introducing the metal for the construction of apparatus required in industrial chemistry. The name is from the Spanish word *platina*, the diminutive of *plata*, silver.

Occurrence.—Like gold, this element occurs widely distributed in nature, but nowhere is it found accumulated in large quantity. It is generally found in the form of the so-called platinum ores, which are alloys of platinum with the other metals considered in this chapter, and in which gold, silver, copper, and iron frequently exist. It is, however, usually the chief constituent. These ores are almost entirely found in alluvial soil, and in the sand of rivers, usually in small steel-gray, flattened or angular grains, and seldom in larger or definitely crystallized masses.

The main deposits are in the Urals, particularly on the eastern slope, in South America, Borneo, Australia, Mexico, and California.

Commercial gold and silver often contain small quantities of platinum.

Preparation.—The method which was formerly used for the purification of native platinum was suggested by Wollaston. It consisted in treating the crude metal first with nitric acid, then with hydrochloric acid, and afterwards with boiling nitro-hydrochloric acid. The last solvent dissolves the platinum, palladium, and a portion of the rhodium, and leaves undissolved a mixture

of osmium, iridium, ruthenium, and rhodium, known as *osmiridium.* The platinum is thrown down from the solution by ammonium chloride as the double chloride of platinum and ammonium. This, when ignited, leaves the metal in a finely-divided state known as *spongy platinum.* The last substance is compressed into a cake by powerful pressure, and is then welded at a white heat into a homogeneous mass. Deville's method, however, has almost entirely superseded that just mentioned. In this the platinum ore is melted with an equal weight of galena and half its weight of metallic lead. The platinum is thus taken up by the lead while the osmiridium remains unattacked. The platinum-lead alloy is then melted and exposed to a current of air, by which the lead is oxidized, the oxide flowing off as slag and the platinum being left as a porous mass. This is placed in a furnace made of lime, and melted by means of a powerful oxyhydrogen blow-pipe flame.

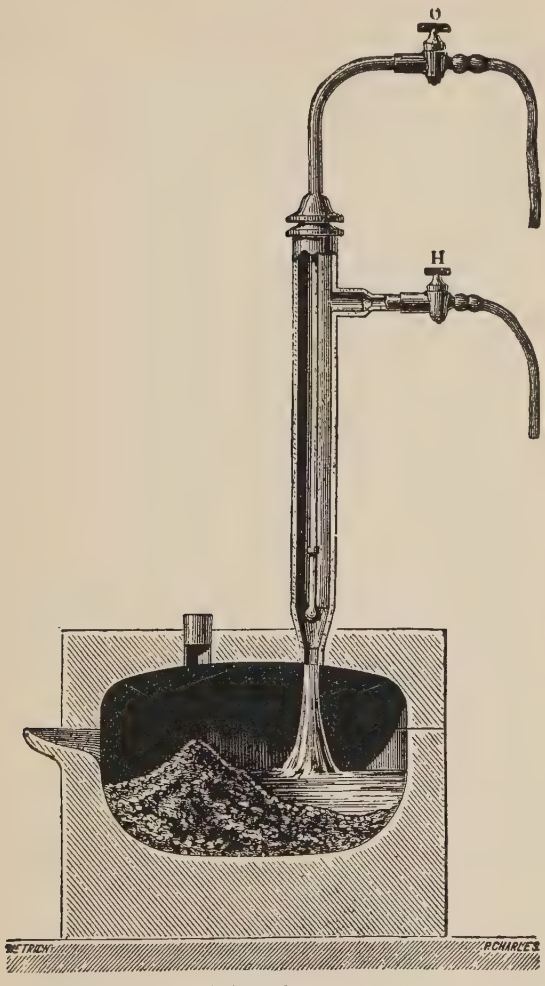
The accompanying figure shows the apparatus used for this purpose. The nozzle of the oxyhydrogen blast-lamp is introduced through a perforation in the dome of the furnace, through which, also, another opening is made for the introduction of the porous metal. From the lip-shaped exit at the side the melted metal may be poured into moulds.

Properties.—In the compact state platinum is of white color It possesses a decided metallic lustre, great malleability, susceptibility of polish, and solidity. Next to gold and silver it is the most ductile of metals. Its malleability is considerably lessened by contamination with other metals, and is particularly noticeable in commercial platinum which contains iridium. Platinum belongs to the most difficultly fusible metals. Except in a very attenuated state and in small quantity, it requires the heat of the oxyhydrogen flame or the flame from the combustion of coal-gas in oxygen to melt it. Deville placed its melting point at 2000°. Like iron it can be welded at a white-heat. It crystallizes in cubes and octohedra. The specific gravity of the melted metal is 21.15, of the hammered metal 21.45. At no temperature does it combine with oxygen. Like copper and silver, the melted metal possesses the property of absorbing oxygen, which, as the metal is allowed to cool, is given off, causing the phenomenon of "spitting."

Compact platinum does not absorb oxygen, but it condenses this gas on its surface, and partly changes it to ozone. This occurs even at 50°.

The strongly oxidizing action of the metal in such a condition may be conveniently illustrated by heating a small piece of platinum foil in the flame of a Bunsen burner, and then quickly ex-

FIG. 143.



Platinum furnace.

tinguishing the flame, allowing the gas to escape. The foil glows, and if placed near the burner it becomes hot enough to inflame the gas. That this property is due to surface action seems to be proved by the fact that the more finely-divided forms of the metal,

platinum-black and *spongy platinum*, possess the same properties to still higher degrees.

Platinum absorbs hydrogen at a red heat and holds it at ordinary temperatures, but at a red heat *in vacuo* the gas is given off. When platinum is employed as the negative pole in the electrolysis of water, it takes up hydrogen, which it will again give up by the employment of the hydrogen-laden metal as positive pole.

When platinum is reduced from its chlorine compounds it is obtained in an extremely finely-divided condition, and is then known as *platinum-black*.

This reduction may be brought about by the action of metallic zinc, or by boiling the solution with an alkali hydrate or carbonate and adding some organic substance, such as sugar or alcohol. In the form of platinum-black, the metal is capable of condensing several hundred times its volume of oxygen. It thus becomes an energetic oxidizing agent ; alcohol thrown upon it is at once ignited. Some authorities regard platinum-black as an oxide. It is a black, hard powder, which, by great pressure and rubbing, may be made to assume a white color. Repeated heating reduces its power to condense oxygen.

Under no circumstances does platinum decompose water. Hydrochloric, hydrofluoric, nitric, and pure sulphuric acids singly do not attack platinum.

Nitro-hydrochloric acid easily and completely dissolves it.

When alloyed with silver it is dissolved by nitric acid.

Fused alkali sulphides, hydrates, cyanides, and nitrates all attack the metal. It is also affected by the free elements or by mixtures which liberate the halogens. Platinum-ware should never be heated in the inner cone of a Bunsen-burner flame, as it is likely to combine with the carbon of the gas to form a compound which injures the texture of the metal. Platinum vessels are usually cleaned by rubbing with moistened round sea-sand, or by fusing in them a quantity of acid potassium sulphate until white fumes of sulphur trioxide are evolved.

Platinum-sponge finds use in Döbereiner's tinder-box, in which nascent hydrogen is inflamed by passing over the porous metal.

Platinum is made into stills for use in distilling sulphuric acid.

The metal was at one time used in Russia for the coinage of money.

The production of platinum in Russia for the year 1895 was 4413 kilos.

When iridium is present in platinum it does not disqualify it for the preparation of apparatus, but, on the contrary, better adapts it for such purposes, inasmuch as it makes the articles less fusible, more rigid, harder, denser, and less readily attacked chemically than pure platinum. An alloy of 8 parts of platinum and 2 parts of iridium is only very slightly dissolved by nitro-hydrochloric acid. An alloy containing 10 per cent. of iridium was used in France to prepare the standard metre and kilogramme.

Porcelain is ornamented with platinum by applying a thin paste made from platinum and ammonium chloride by the aid of rosemary and lavender oils, the article being subsequently heated in a muffle. To coat metallic objects, a paste of the same salt but with tartaric acid, or the metal in the form of a very thin foil, is strongly rubbed on, or the article may be suspended in a regular plating bath of the double chloride dissolved in a solution of sodium carbonate.

PLATINUM AND THE HALOGENS.

Platinous Chloride, $PtCl_2$, is obtained by heating spongy platinum in a stream of dry chlorine to 240°–250°.

It is a gray-green powder, insoluble in water, but soluble in hot hydrochloric acid to give a red-brown colored solution.

Chloroplatinic Acid, $PtCl_4, 2HCl.6H_2O$, results when platinum is dissolved in nitro-hydrochloric acid and the solution evaporated with hydrochloric acid to expel nitric acid. By completing the evaporation over sulphuric acid or caustic lime a deliquescent salt is obtained.

It is used in platinum-plating and as a reagent for potassium.

Platinic Chloride, $PtCl_4.5H_2O$.—When a molecule of chloroplatinic acid is decomposed with two molecules of silver nitrate and the resulting precipitate filtered off, a yeliowish-red, silver-free solution is obtained, which, upon evaporation, yields platinic chloride as a red, crystalline, non-deliquescent salt.

Both chloroplatinic acid and platinic chloride form with the chlorides of potassium and ammonium difficultly-soluble, yellow, crystalline, double chlorides. The corresponding sodium and lithium compounds are soluble.

Platinous Bromide, $PtBr_2$, results as a brown-gray, insoluble mass when bromoplatinic acid is heated to 200°.

Platinic Bromide, $PtBr_4$, is not known except in combination with hydrobromic acid as bromoplatinic acid. The latter is produced by dissolving platinum in a mixture of nitric and hydrobromic acids; it crystallizes in deliquescent, dark-red prisms.

Platinous Iodide, PtI_2, is a black powder obtained by warming platinous chloride with potassium iodide.

Platinic Iodide, PtI_4.—By heating an excess of chloroplatinic acid with potassium iodide a black powder, insoluble in water and soluble in potassium iodide, is obtained.

PLATINUM AND OXYGEN.

Platinous Oxide, PtO, and *Platinic Oxide*, PtO_2, are obtained as black powders by careful heating of the respective hydrates.

Platinous Hydrate, $Pt(OH)_2$, forms a black powder which possesses the characters of a weak base. It is obtained by digesting platinous chloride with potassium hydrate.

Platinic Hydrate, $Pt(OH)_4$, is obtained as a white, flocculent precipitate by boiling chloroplatinic acid with an excess of sodium hydrate, and then acidifying the liquid with acetic acid.

Platinous Sulphide, PtS, and *Platinic Sulphide*, PtS_2, are precipitated from the corresponding chlorides when the latter, in water solution, are treated with hydrogen sulphide. They are black-brown powders.

Platinum forms many series of ammonium compounds. Fulminating platinum is produced by decomposing platinum and ammonium chloride with potassium hydrate. It is a straw-colored powder whose composition has not been determined.

RHODIUM.

Symbol, Rh. *Atomic Weight*, 102.9. *Valence*, II and IV.

Wollaston discovered this element in an American platinum ore in 1804, and on account of the rose-red color of its chloride gave to it the name rhodium. Apart from its occurrence in platinum ores, rhodium occurs alloyed with gold. In the compact state it is a gray-white, malleable metal, which is more difficultly fusible than platinum, but more easily than iridium. Its specific gravity is 12.1. It oxidizes superficially, becoming blue when strongly heated in the air or in contact with alkalies. Rhodium is insoluble in all acids with the exception of nitro-hydrochloric. Its alloys are, however, more easily dissolved. At a red heat chlorine produces with the finely-divided metal red, insoluble rhodium chloride, Rh_2Cl_6.

Rhodium gives oxides of the following compositions: RhO, Rh_2O_3, and RhO_2. The hydrates, $Rh(OH)_4$ and $Rh_2(OH)_6$, are known.

RUTHENIUM.

Symbol, Ru. *Atomic Weight*, 101.4. *Valence*, II and IV.

Ruthenium was first observed in 1828, by Osann, in the residues from the working of the Russian platinum ores.

The name ruthenium was applied to the new element because the ores came from Russia. It was first prepared in a pure state by Claus, in 1848.

It also occurs as sulphide in *laurite*, which is found along with platinum ores in Borneo and Oregon.

Ruthenium is a gray-white, brittle metal, which, with the exception of osmium, is the most difficultly fusible of the members of the platinum group.

When melted the metal is somewhat oxidized. The specific gravity of ruthenium is 12.26. The acids, including nitro-hydrochloric acid, fail to dissolve it.

At a low red heat the metal combines with chlorine to give ruthenium dichloride, $RuCl_2$. The other chlorides known are Ru_2Cl_6 and $RuCl_4$.

Besides oxides and hydrates of the same constitution as those yielded by rhodium, ruthenium also forms RuO_2 and RuO_4. By fusing the finely-divided metal with potassium hydrate and potassium nitrate, potassium rutheniate, K_2RuO_4, is obtained. It dissolves in water with a red-yellow color; the solution blackens the skin. Nitric acid throws down from the water solution a black precipitate of ruthenium sesquihydrate, $Ru_2(OH)_6$, which dissolves in hydrochloric acid with an orange-red color.

PALLADIUM.

Symbol, Pd. *Atomic Weight,* 106.35. *Valence,* II and IV.

In 1803 palladium was discovered by Wollaston in native platinum. He named it after the then recently discovered planet Pallas. It is alloyed with platinum in almost all ores in which the last metal is found. To some extent it occurs in the pure state, in the form of small, flattened grains, which are mixed with the Brazilian platinum ores.

A Brazilian gold ore which contains from 5 to 10 per cent. of palladium forms its chief source. In its appearance, lustre, hardness, and malleability this metal is very similar to platinum. It is the most fusible of the platinum metals. Heated in air it becomes superficially oxidized, but at a higher temperature regains its lustre. It has a specific gravity of 11.4.

Hot, strong mineral acids and alkalies attack the metal. This element has an affinity for hydrogen that has characterized it above all others. Palladium hydride, Pd_2H, which contains about 600 volumes of hydrogen, is the product of the union, and is considered to be an alloy of the elements whose formation takes place most favorably at 100°. In forming this compound the metal is said to *occlude* the gas. Palladium generally occurs in commerce in foil. It is used to some extent for the mountings of physical and mathematical instruments and in dental wares.

Of the chlorine compounds of the metal only palladious chloride, $PdCl_2$, is known in the isolated state, although palladic chloride, $PdCl_4$, may result when the metal is dissolved in nitro-hydrochloric acid. When this solution is evaporated chlorine is given off, and brown-red prisms, having the composition $PdCl_2.2H_2O$, are obtained. The aqueous solution of the last salt serves for the quantitative separation of iodine from bromine and chlorine.

IRIDIUM.

Symbol, Ir. *Atomic Weight,* 192.5. *Valence,* II and IV.

Iridium was discovered along with osmium in 1804, by Smithson Tennant, in the *osmiridium* left in the working of platinum ores. On account

of the manifold colors which the solution of its chloride showed, he designated it by its present name. Besides the above source it is sometimes found alloyed with platinum alone. Iridium forms in the compact state a pure white, steel-like, lustrous, brittle metal. It is harder and less fusible than platinum, and has a specific gravity of 22.4. It behaves somewhat like palladium when heated in air or oxygen. In the compact state it is insoluble in all acids. Only in the divided state is it soluble in nitro-hydrochloric acid to give iridium tetrachloride, $IrCl_4$.

The oxides and hydrates of iridium have the following formulas: IrO, Ir_2O_3, IrO_2, $Ir(OH)_2$, $Ir_2(OH)_6$, and $Ir(OH)_4$. They are all recognized as compounds having weak properties both as acids and bases. Their salts are but little known. Platinum is alloyed with iridium to increase its resistance to chemicals. It is used to tip gold pens, which are thereby rendered much more durable. To impart a black color, both the finely-divided metal and the sesquioxide are used in porcelain decorations.

OSMIUM.

Symbol, Os. *Atomic Weight,* 190.3. *Valence,* II and IV.

Osmium was discovered in 1804, by Smithson Tennant, along with iridium, in the *osmiridium* or insoluble residue left upon treatment of the platinum ores with nitro-hydrochloric acid.

The name is from the Greek word ὀσμή, meaning odor.

The metal, when finely powdered, emits a peculiar, pungent, iodine-like odor, in consequence of the formation of osmic anhydride, OsO_4. Osmium is the heaviest metal known, having the specific gravity of 22.47. It is hard, bluish-white, and volatile at the temperature of melting iridium It has never been melted. The metal combines with chlorine to give *osmium dichloride*, $OsCl_2$, and *tetrachloride*, $OsCl_4$. *Osmium sesquichloride*, Os_2Cl_6, is not known in the free state.

The following oxides and hydrates are known: OsO, Os_2O_3, OsO_2, OsO_4, $Os_2(OH)_6$, and $Os(OH)_4$.

Fuming nitric acid and nitro-hydrochloric acid convert osmium into osmic anhydride, OsO_4, which is also produced by melting the metal with potassium nitrate. Osmic anhydride forms colorless, glistening needles, which volatilize without decomposition. The vapors emitted by this substance are irritating to the eyes and suffocating. It is soluble in water, giving a colorless, neutral solution, which has a caustic taste and the peculiar iodine-like odor of the anhydride.

Osmic anhydride is an oxidizing agent. It is used as a stain in histological work. Osmic acid, H_2OsO_4, is not known in the free state.

When alcohol is added to a solution of the anhydride in potassium hydrate a reddish precipitate of potassium osmate, $K_2OsO_4.2H_2O$, is thrown down.

The great hardness of osmiridium is taken advantage of for cutting glass, as also for the manufacture of the points of writing pens.

PART IV.

ORGANIC CHEMISTRY.

CHAPTER I.

INTRODUCTORY.

1. Distinction between Organic and Inorganic Compounds.—It becomes necessary at the beginning of this section of chemistry to give a reason for the separation of carbon compounds from those of the other elements. Such a reason seems to be found in the use of the terms *organic* as applied to the chemistry of the carbon compounds, and *inorganic* as applied to the chemistry of the other elements. The organic compounds—that is, those belonging to the vegetable and animal kingdoms—are undoubtedly produced in the presence of and often as a result of the functions of vegetable and animal life, while the inorganic compounds, found mainly in the mineral kingdom, represent simply the result of the action of the laws of chemical attraction. Berzelius and the older chemists therefore made the sharp distinction that organic compounds were produced in some way under the influence of plant or animal vitality and could not be made artificially in the laboratory, while inorganic compounds could be built up artificially by appropriate chemical reactions. This distinction no longer exists. It was first broken down by the synthesis on the part of Wöhler, in 1828, of urea, a typical secretion of the animal organism, followed later by that of acetic acid and other so-called organic compounds. The number of plant and animal principles or secretions that have been made synthetically is so large that we can no longer believe that the influence of plant or animal life is essential for their formation. The same chemical forces undoubtedly act in both the organic and the inorganic worlds.

The separation of the carbon compounds from those of the other elements, which is still maintained in most chemical text-books, is therefore at present mainly a matter of convenience.

Owing to the peculiar tendency of the carbon atoms to aggregate together in groups and the facility with which the saturating hydrogen of "hydrocarbons," as the combinations of these two elements are called, is replaced, the number of carbon compounds capable of formation is an immense one. Besides the many thousands of these carbon compounds naturally occurring, the number artificially formed has grown enormously in recent years. It becomes eminently desirable, therefore, to classify them and study them apart from the compounds of the other elements.

2. Composition and Analysis of Organic Compounds.—Many organic compounds contain carbon and hydrogen only, and are known as "hydrocarbons." The other elements found at times as constituents of organic compounds are oxygen and nitrogen, and less frequently sulphur and phosphorus. The halogens and other elements are often introduced by substitution into the formulas of organic bodies.

The analysis of the carbon compounds may be either *qualitative* or *quantitative*, and both of these methods may be applied with reference to the *ultimate* (or *elementary*) and the *proximate* composition of the substance analyzed.

(*a*) *Qualitatively*, carbon is shown in many cases by the charring which takes place when the substance is heated on a strip of platinum foil. In case the material is volatile without decomposition, it is mixed with easily reducible substances, such as copper oxide or chromate of lead, placed in a tube sealed at one end, and heated, when the carbon is oxidized to carbon dioxide. The escaping gas may be conducted through lime-water, and the presence of carbon will be indicated by the turbidity produced in this.

The same mixture of the suspected organic compound with oxide of copper or chromate of lead when heated will give rise to the formation of water if hydrogen is present. This will condense in the cooler part of the tube or may be received in a tube containing calcium chloride.

The nitrogen in many organic compounds is indicated by the decomposition on heating with evolution of the odor of burnt feathers. Such substances heated in a tube closed at one end with soda-lime (a mixture of caustic soda with lime) will give off ammonia, readily recognizable by its odor or by the use of red litmus paper. Some nitrogenous compounds do not respond to this test. A test applicable, however, to all organic nitrogenous compounds is to heat the substance in a small dry test-tube with

a fragment of metallic sodium or potassium, and to test the metallic cyanide formed by dissolving the melted mass in water, filtering, heating with a few drops of ferrous sulphate and caustic soda solutions, and then adding ferric chloride. On the addition of hydrochloric acid, a precipitate of Prussian blue is obtained if nitrogen were originally present.

The halogens cannot always be detected by the direct addition of silver nitrate solution. If the substance, however, be ignited with quick-lime, the haloid calcium salt so formed can be tested for with silver nitrate. Or the substance may be mixed with pure copper oxide and ignited on a loop of platinum wire. A blue color changing to green appearing in the flame will indicate chlorine, and a green color iodine. Still another method consists in heating the substance with fuming nitric acid and silver nitrate in a sealed tube, when the haloid silver salt is produced. Sulphur can be detected by ignition with sodium, forming sodium sulphide, which is then dissolved out and tested for with sodium nitroprusside, yielding a purple coloration.

Or the substance may be oxidized either, in case it be a solid, with a mixture of potassium hydrate and nitre, or, in case it be a liquid, with fuming nitric acid. The sulphur is thus converted into sulphuric acid, which is then tested for with barium chloride.

Phosphorus is also capable of oxidation into phosphoric acid by the same means, and this can then be tested for as usual with sodium molybdate. Ignition with powdered magnesia will cause the formation of a phosphide which on moistening with water will evolve phosphoretted hydrogen.

All other elements, after complete oxidation of the organic compound as above, may be tested for by the methods of inorganic chemistry.

(*b*) *Quantitatively* carbon and hydrogen are always determined together by what is termed an organic combustion. In this case a weighed quantity of the substance is heated in a tube of difficultly fusible glass along with an easily reducible substance like oxide of copper or chromate of lead. The carbon is oxidized to carbon dioxide and the hydrogen to water, both of which are to be collected in weighed absorption vessels. The increase in weight of these allows of a determination of the amount of carbon and hydrogen respectively present in the substance burned. The arrangement of the apparatus and the combustion furnace are shown in Fig. 144. Either a tube sealed at one end may be used, in which case the sealed end is drawn out to a fine point so that

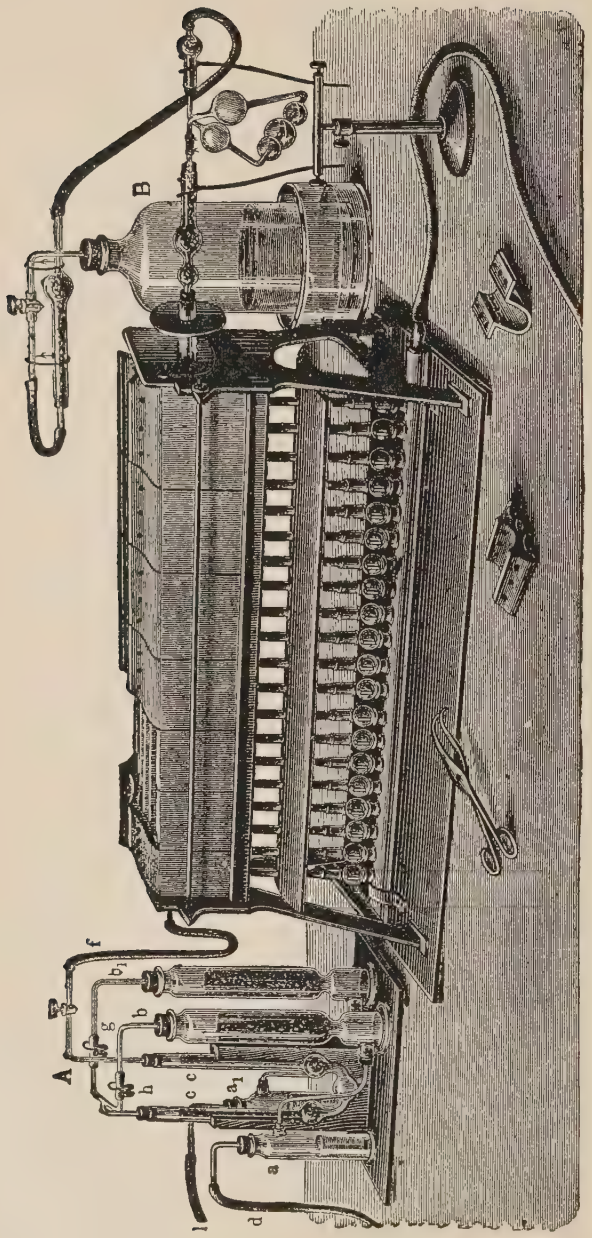
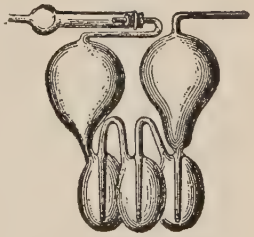


FIG. 144.

Gas combustion furnace.

at the end of the heating it may be broken and a current of purified air or oxygen passed through, or a tube open at both ends is taken. In the latter case the combustion is carried out from beginning to end in a current of purified oxygen. The purification of the oxygen or of a current of air is effected in the apparatus shown in the cut as connected with the rear end of the combustion tube. Oxygen entering through the tube *d* passes through sulphuric acid in *a*, a chloride of calcium jar at *b*, and a U tube filled with stick potash at *c c*, and then through the tube *f* to the combustion tube. A second series of absorption vessels on the same stand serves for air. The water produced by the oxidation of the hydrogen of the organic substance is caught in a weighed tube containing fused and granulated chloride of calcium, and the carbon dioxide produced by the oxidation of the carbon of the organic substance is caught in a weighed bulb apparatus containing strong caustic potash solution. Instead of the older form of potash bulbs known as the Liebig bulbs shown in Fig. 144, the apparatus of Geissler shown in Fig. 145 is now more generally used because of the convenience in weighing. One-ninth of the increase of weight of the chloride of calcium tube represents the weight of the hydrogen, while three-elevenths of the increase of weight of the potash bulbs represents the weight of the carbon.

Fig. 145.



Geissler's potash bulbs.

If the organic compound is nitrogenous, a spiral of metallic copper or silver must be placed in the front end of the combustion tube and kept at a low red heat in order to prevent the oxides of nitrogen from going over in the absorption apparatus and vitiating the results. Organic compounds containing sulphur must be burned with chromate of lead, which will oxidize the sulphur and hold it as sulphate of lead. Halogens present in an organic compound are held as silver haloid salts by the use of the silver spiral before alluded to.

The nitrogen of an organic compound is either determined absolutely and its volume measured, or it is converted into ammonia by combustion with soda-lime as in the Will-Varrentrap method, or by heating with strong sulphuric acid and potassium permanganate as in the Kjeldahl method. In the determination of nitrogen by volume a tube closed at one end is used, and in

the farther end sodium bicarbonate or magnesite is placed. This is first heated so as to displace all the air of the tube by carbon dioxide, and then the substance is burned with copper oxide, a copper spiral being used of course in the front end of the tube to decompose oxides of nitrogen. The nitrogen gas is collected over strong potash solution, which absorbs the carbon dioxide and allows of the measurement of the volume of residual nitrogen. In the soda-lime process the substance is burned in a tube closed at one end, somewhat shorter than the ordinary combustion tube, and the ammonia produced is absorbed in pure strong hydrochloric acid. We may then either determine the ammonia here caught as sal ammoniac by the use of platinic chloride, or, if a measured amount of hydrochloric acid of known strength was taken, may titrate back with normal alkali solution and so determine the ammonia indirectly. In the Kjeldahl process the substance is heated with concentrated sulphuric acid for some time to a temperature near the boiling point of the latter, the addition of small portions of powdered potassium permanganate near the end of the action sufficing to complete the ammonia formation. The mixture is then diluted with water, supersaturated with caustic soda, and the ammonia distilled off and determined volumetrically.

The methods for the determination of the halogens, sulphur, and phosphorus have already been indicated in speaking of their qualitative detection.

Oxygen is always determined by difference, as no reliable general method for its determination exists.

3. Physical Properties of Organic Compounds.—The physical properties are just as important points for observation in the case of organic compounds as with inorganic substances, only, instead of crystalline form, hardness, lustre, color, etc., the important properties for consideration in this connection are fusing point, boiling point, vapor-density, and in some cases optical properties.

(*a*) *Fusing Point.*—Most organic solids, when sufficiently pure, fuse either with or without decomposition at a constant temperature. To determine the fusing point, a small quantity of the substance carefully dried and pulverized is placed in a capillary tube sealed at one end, and this is attached by a rubber band to a thermometer in such a way that the capillary tube with the substance is immediately adjacent to the bulb of the thermometer. A round-bottomed flask with a long neck is then taken, and in this is placed concentrated sulphuric acid or paraffin so that the

bulb of the flask is three-quarters full. The thermometer with capillary tube attached is held in position by passing it through a perforated cork fitted in the neck of the flask, and dips into the liquid far enough to allow the bulb and substance in the capillary to be covered. A small side tube fitted in the perforated cork allows the air to escape when the flask is heated. The heat is applied gradually, and the moment the substance in the capillary is in clear fusion the temperature is read off.

(*b*) *Boiling Point and Practical Distillation.*—Most organic liquids boil without decomposition at a fixed temperature, which is called their boiling point. Even in the case of such liquids as cannot be distilled without decomposition under ordinary atmospheric pressure, it is often possible by distilling them under reduced pressure or in vacuo to get them to vaporize at a constant temperature. A boiling point, constant for the same atmospheric pressure, is taken as one of the most reliable indications of purity and identity of organic liquids.

To determine the boiling point the liquid is placed in what is termed a distillation bulb. This consists of a bulb with tall narrow neck into the side of which at some height above the liquid is fused a delivery tube bending downward at an oblique angle. The neck of the distillation bulb is closed by a tight-fitting cork perforated for a slender thermometer. The latter must extend so far into the neck that the mercury bulb comes just below the lateral exit for the vapors, but never dip into the liquid. If in making a boiling-point determination any part of the mercury column extends above the neck of the distillation bulb where it is surrounded by vapor, a correction must be made depending upon the length of the column not surrounded by vapor. Of course, the boiling point is always dependent upon the atmospheric pressure, as indicated by the barometer (see page 48), and therefore the pressure must be noted in connection with each boiling-point determination.

A mixture of organic liquids of different boiling points can often be separated into its components by what is termed fractional distillation, especially when the boiling points of the individual components are moderately removed from each other. In this case fractions of the distillate are caught separately at fixed intervals, say every five or ten degrees, and these are then distilled by themselves and the portions coming over at approximately the same temperature added together. By repeating the operation several times the distillates show a tendency to accumulate at a

few fixed temperatures corresponding to the boiling points of the components of the original mixture.

The process of fractional distillation is much facilitated by the use of distillation bulbs with special arrangements for condensation in the vertical neck attached to the bulb or flask, such as the apparatus of Wurtz, Linnemann, and Hempel. These accomplish a fractional condensation of the vapors corresponding to that effected in the column apparatus of the rectifier or tar distiller.

(*c*) *Determination of Molecular Weight.*—This determination has considerable importance in the study of organic compounds, as, for reasons to be explained later, ultimate organic analysis does not generally enable us definitely to determine molecular weight and molecular formulas. Three methods for determining the molecular weights of bodies may be noted :

1. Measuring the vapor-density.

2. Raoult's method of measuring the lowering of the freezing point of a solution.

3. Beckmann's method of measuring the elevation of the boiling point of a solution.

1. For determination of *vapor-density* we can ascertain the weight of a definite volume of the vapor, which is then compared with the weight of the same volume of air under similar conditions of temperature and pressure, or the volume occupied by the vapor obtained from a fixed weight of the substance, or thirdly, the volume of another substance like mercury or air displaced by the vapor from a definite weight of the compound under investigation.

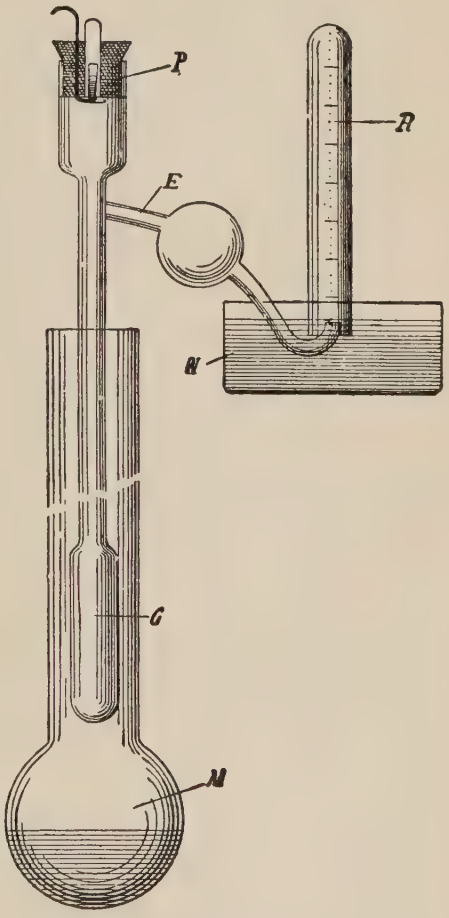
To the first class of determinations belongs the Dumas vapor-density method, in which globes of heavy glass with narrowed neck are used. These are weighed full of the vapor after the neck has been sealed by fusion of the capillary portion, and then opened under mercury so that the cubic contents of the globe can be accurately determined by measuring the mercury which fills it. The method is now rarely used.

To the second class of determinations belongs the Hofmann vapor-density method. In this case we have a tall barometer tube filled with mercury and dipping into a mercury trough. This is surrounded by a wider mantle-tube through which the vapor of water, aniline, or other higher-boiling liquid may circulate. Before the vapor is made to pass through the mantle, the weighed portion of the substance whose vapor-density is required is passed up into the barometer tube. Here, as the tube becomes heated by the vapor surrounding it, the substance vaporizes in

vacuo. When the level of the mercury becomes constant in the tube, it is read off and the volume of vapor is calculated.

To the third class of determinations belongs the method of Victor Meyer, which is at the present time in most general use. The apparatus for this is shown in Fig. 146. The vessel in which the substance is to be vaporized is shown at G. This is closed by a cork perforated and fitted with a glass tube in which the little vessel with substance is placed as shown at P. The liquid in the mantle at M is first brought to boiling, and when air ceases to issue through the delivery tube at E, the eudiometer tube R is placed in position over the end of the delivery tube as shown in the illustration. The little tube containing the substance is then caused to fall by bending the wire support to one side. The vapor of the organic compound displaces an amount of air corresponding to its volume at the temperature of the experiment. Not more than 0.1 gramme of the substance is needed for this method. From the results of this determination, the vapor-density is calculated by the use of the following formula: $D = \frac{S.760(1.003665t)}{V.(B-w)0.001293}$, in which D stands for density, S for weight of substance, t for temperature.

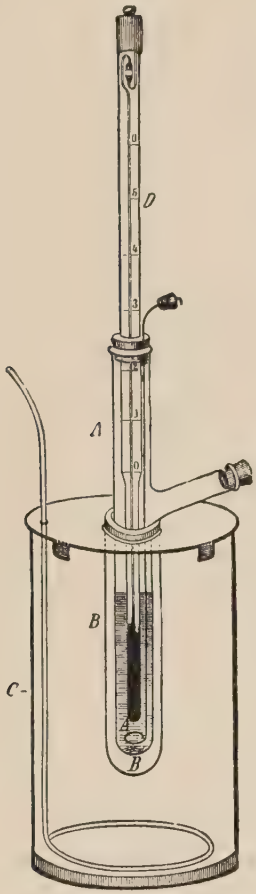
FIG. 146.



Victor Meyer's vapor-density apparatus.

V for volume of air displaced, B for barometric reading, and w for tension of the vapor of water at the temperature of the observation. Inasmuch as air is 14.435 times heavier than hydrogen, the value D must be multiplied by 14.435 to obtain vapor-density based on hydrogen, and by 28.87 to get the molecular weight of the substance used.

Fig. 147.



Beckmann's apparatus.

2. The researches of Raoult (1882) have established the fact that when a known amount of a substance is dissolved in a measured quantity of a solvent (such as benzene or glacial acetic acid) the lowering of the freezing point of the latter produced by the presence of the former is a function of the molecular weight of the dissolved substance. The formula used is $M = c\frac{p}{t}$, where M is the molecular weight, c the constant for the liquid used, p the percentage of the substance contained in the solvent, and t the depression of the freezing point in degrees Centigrade.

The constants for the solvents most commonly used are found to be :

Benzene	49	Diphenylamine .	88
Glacial Acetic Acid	39	Naphthalene . .	69
Nitrobenzene . . .	71	Naphthylamine .	78
Phenol	74	p-Toluidine . .	51
Water	18.9	Thymol	92

A comparison of these constants shows that they bear the same ratio to each other as the molecular weights of the substances used as solvents.

For the carrying out of this determination Beckmann's apparatus, shown in Fig. 147, is generally used. A glass tube, A, with a side projection, is filled with 15–20 grammes of the solvent (weighed accurately, however) and closed with a cork in which are placed an accurate thermometer, capable of adjustment for use at different temperatures and divided into hundredths of a degree, and a

stout platinum wire, serving as a stirring-rod. This tube is placed in a somewhat wider tube, B, which serves as an air-jacket. The whole is suspended in a wide battery-jar, C, which contains cold water or a freezing mixture, the temperature of which should be from 2° to 5° below the freezing point of the solvent.

The congealing point of the solvent is first determined by cooling it several degrees below its freezing point, and then by agitation with the platinum rod (after adding platinum clippings) the formation of crystals is started. During this formation the temperature rises, and when the mercury becomes stationary, it indicates the exact freezing point of the solvent. After the mass has melted again, an accurately weighed amount of substance is introduced through E. When this has dissolved, the freezing point is redetermined as before.

3. Beckmann has also worked out a method by which the elevation in the boiling point of a liquid produced by dissolving any substance in it can be used for the determination of the molecular weight of the substance. The formula used is $M = c\frac{g}{G(t'-t)}$, where M is the molecular weight, c the constant indicating the molecular elevation of the boiling point for 100 grammes of the solvent, g the weight of the substance, G the weight of the solvent, t the boiling point of the solvent, and t' the boiling point of the solution.

The boiling points and constants of the solvents used are as follows:

Solvent.	Boiling Point.	C.
Glacial Acetic Acid	118.1	25.3
Acetone	56.3	16.7
Aniline	183.0	32.2
Benzene	80.3	26.7
Carbon Disulphide	46.2	23.7
Chloroform	61.2	36.6
Ethyl Alcohol	78.3	11.5
Ethyl Ether	35.0	21.1
Methyl Alcohol	66.0	9.2
Phenol	183.0	30.4
Water	100.0	5.2

(*d*) *Optical Properties.*—Many organic compounds turn the plane of polarization of light. This may happen with the bodies in the solid state, as with benzile, $C_{14}H_{10}O_2$, or with others when

solid as well as when in solution, as with strychnine sulphate; but most generally it is shown in liquids only, as tartaric acid and the sugars. Some liquids, like oil of turpentine, also show it in their vapors.

In many cases several optically active modifications of the same compound exist. Thus, a dextro-rotatory and a lævo-rotatory modification can be obtained, as in the case of tartaric acid. These will combine to form an inactive variety of the same compound. Conversely, the inactive variety can often be broken up into the two optically opposed varieties. This may be done in several ways. Inactive tartaric (racemic) acid may be transformed into the ordinary active variety by heating to 170° C., or the salts of the inactive acid will crystallize out as a mixture of the two opposing varieties. The addition of certain ferments will also cause a change of an inactive variety into an active one.

The angle of rotation of the plane of polarized light in the case of an optically active substance is proportional to the thickness of the layer traversed. It is also dependent upon the wave-length of the light used for illumination in the instrument. Yellow monochromatic light from a sodium flame is generally used. It is also somewhat dependent upon temperature.

When the specific rotatory power of a substance is known, we can, in the case of a solution containing this substance as the only optically active ingredient, determine the percentage of material present from an observation of the angle of actual rotation. Thus, in the case of a sample of diabetic urine, we have observed an actual rotation of $+1.5°$. Knowing the specific rotatory power of grape sugar to be 52.5° we make the calculation $p = \frac{100 \times 1.5}{52.5 \times 1} = 2.8$ per cent. grape sugar. In case the specific gravity of the solution is much over 1, that must also be used, multiplying it into the denominator. The practical use of the polariscope will be referred to again under *Sugars*.

An explanation of the optical activity of organic compounds has been offered in recent years by Le Bel and Van t'Hoff. This is that optically active compounds contain one or more *asymmetric* carbon atoms—that is, carbon atoms each of the four affinities of which are joined to a different atom or group, as in the case of optically active amyl alcohol, $H—\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}—C_3H_7$. It has been found

that all optically active substances contain such asymmetric carbon atoms, but the converse is not invariably true.

4. Isomerism and Structural Formulas.—The results of an ultimate combustion analysis of an organic compound will give us nothing more than the ratio of the atoms composing it. Even with the molecular weight obtained by means of a vapor-density determination, we can give only what is called an *empirical* formula; that is, one which expresses the number of the several atoms present but with no information as to how they are joined together. We find, however, that there are numerous cases where several bodies may exist having the same percentage composition, or even the same absolute number of the constituent atoms, and yet be quite different in physical properties. Thus, CH_2O, formaldehyde, $C_2H_4O_2$, acetic acid, and $C_3H_6O_3$, lactic acid, will have the same percentage composition although of different formulas. Again, pyrocatechin, resorcin, and hydroquinone all have the formula $C_6H_6O_2$ and yet are quite distinct in fusing points as well as in chemical reactions.

Bodies which have such points of agreement and yet are different are said to be *isomeric*.

We may distinguish four distinct cases of *isomerism*.

(*a*) When the isomeric bodies have the same percentage composition but a different molecular weight. Such bodies are said to be *polymeric*. Thus, C_2H_4, ethylene; C_3H_6, propylene; C_4H_8, butylene; C_5H_{10}, amylene, are polymeric, the unit of increment being CH_2. CH_2O, formaldehyde; $C_2H_4O_2$, acetic acid; $C_3H_6O_3$, lactic acid; $C_6H_{12}O_6$, grape sugar, are also polymeric.

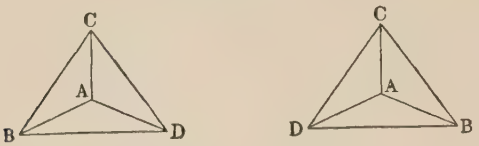
(*b*) When the isomeric bodies have the same molecular weight also. Such bodies are said to be *metameric*, as their difference is based upon a different arrangement of the atoms within the molecule. Thus, trimethylamine and propylamine have equally the formula C_3H_9N; methyl ether and ethyl alcohol have equally the formula C_2H_6O; dextrose and levulose have equally the formula $C_6H_{12}O_6$.

(*c*) A third case of isomerism is what is termed *physical isomerism*. This is believed to be due to a different geometrical position of the atoms in the molecule, as explained in the new stereochemical theories. These theories, which were first proposed by Van t'Hoff and developed by Wislicenus, may be briefly stated as follows:

If a carbon atom is combined with four different atoms or

atomic groups no case of isomerism can arise on the ground of difference in chemical constitution, as in the class just mentioned. Yet different tetra substitution derivatives may exist in some cases. These are explained by noting the difference between a positive and a negative tetrahedron, as shown in Fig. 148.

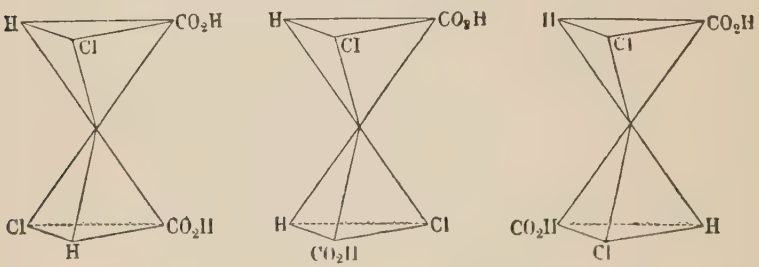
FIG. 148.



One of these figures is the reciprocal or reflection of the other. If we suppose the tetrad carbon atom to be in the centre of such a tetrahedron and the four saturating atoms or groups at the four angles, we will have in the two forms of tetrahedra illustrations of the two possible molecules. One of these may be optically dextro-rotatory and the other lævo-rotatory, as in the case of the two varieties of tartaric acid.

Again, if two such carbon atoms are linked together by the sacrifice of one bond on the part of each carbon, we may suppose a certain rotation around this point of juncture possible, and may have the cases of difference in the molecules indicated in the several graphic illustrations shown in Fig. 149.

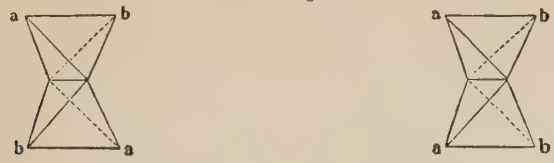
FIG. 149.



If two carbon atoms are united by the union of two bonds on the part of each carbon, there is no longer any rotation possible, such as shown in the preceding cases. But the two tetrahedra may be differently joined, as shown in Fig. 150.

In illustration of this form of difference we can take the example of fumaric and maleic acids, which are considered

FIG. 150.



to differ from each other by the stereo-chemical distinction expressed in the formulas

$$\begin{matrix} CH{-}COOH \\ \| \\ CH{-}COOH \end{matrix} \quad \text{and} \quad \begin{matrix} CH{-}COOH \\ \| \\ COOH{-}CH. \end{matrix}$$

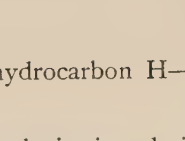
(*d*) We have yet the case of isomerism based upon change in the method of linking the hydrogen in the molecule. Such bodies are called *tautomeric*. Thus, the formula of hydrogen cyanide may be $N{\equiv}C{-}H$ or $C{\equiv}N{-}H$, and two series of derivatives readily changing into each other are formed, the cyanides and the isocyanides, according as one or the other molecular grouping exists.

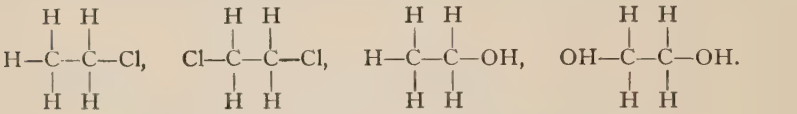
Formulas which show the method of the linking of the constituent atoms are called *rational* or *structural* formulas. Their importance in organic chemistry, where differences in compounds may depend, as shown above, on the variations in the method of linking the elements, is obvious.

The tetrad character of the carbon element, to start with, is represented thus : $\begin{matrix} | \\ {-}C{-} \\ | \end{matrix}$. When these four bonds of the carbon are satisfied with hydrogen we have the fundamental hydrocarbon $\begin{matrix} & H & \\ & | & \\ H{-}C{-}H, & & \text{methane.} \\ & | & \\ & H & \end{matrix}$ The hydrogen atoms are readily replaceable by monad atoms and groups, and the substitution compounds so formed will be represented thus :

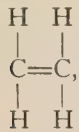
$$\begin{matrix} H \\ | \\ H{-}C{-}H, \\ | \\ Cl \end{matrix} \qquad \begin{matrix} I \\ | \\ H{-}C{-}I, \\ | \\ I \end{matrix} \qquad \begin{matrix} H \\ | \\ H{-}C{-}OH, \\ | \\ H \end{matrix} \qquad \begin{matrix} H \\ | \\ H{-}C{-}NH_2. \\ | \\ H \end{matrix}$$

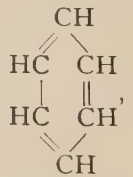
Several carbon atoms may be joined together by the aid of one or more bonds furnished by each of the carbon atoms. Thus,

we have the hydrocarbon  , ethane. In this case and in all its substitution derivatives the use of the structural formula becomes of great assistance in showing the nature and relationship of the molecule. We have among these derivatives



A more condensed form of rational formula is sometimes employed, as $CH_3.CH_2Cl$, $CH_2Cl.CH_2Cl$, $CH_3.CH_2OH$, $CH_2OH.CH_2OH$, in which the saturation of each individual carbon atom is shown without the aid of the graphic formulas showing the bonds.

In  , ethylene, we have indicated a double linking of the carbon atoms, and in acetylene, a treble linking. The hydrogen atoms of these compounds are of course replaceable by monad atoms or groups, as in the case of hydrocarbons with the single linking.

Still more important becomes the structural formula in the case of the benzene derivatives or aromatic compounds. Here the fundamental hydrocarbon benzene is represented,  , that is, six carbon atoms alternately singly and doubly united, so that each carbon atom sacrifices three bonds in the linking of the molecule and has one free for combination with hydrogen or its equivalent replacing group.

Such a method of linking is generally known as the "closed-chain" structure, in distinction from the "open-chain" structure before shown with ethane and similar hydrocarbons.

5. Radicals, Residues, and Atomic Groups.—The residue

remaining after taking away one or more atoms from an organic compound is often called a *radical.* The valence of this radical or residue depends upon the number of hydrogen atoms which must be added to make a saturated compound of it.

The relative importance of these radicals in the study of organic compounds is so great that at one time organic chemistry was defined as the "chemistry of compound radicals."

Thus, by the withdrawal of one hydrogen atom from the saturated hydrocarbon methane, CH_4, we obtain the monad radical methyl, CH_3; by the withdrawal of two hydrogen atoms we get the dyad radical methylene, CH_2; by the withdrawal of three hydrogen atoms we get the triad radical methenyl, CH. Similarly, from ethane, C_2H_6, we get the monad radical ethyl, C_2H_5, and from propane, C_3H_8, we get the monad radical propyl, C_3H_7. These radicals are then very conveniently written as units in the rational formulas of organic compounds, as $CH_3.Cl$ and $CH_3.OH$, known as methyl chloride and methyl alcohol respectively, or $C_2H_5.Br$ and $(C_2H_5)_2O$, known as ethyl bromide and ethyl ether respectively.

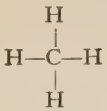
Many of the inorganic groups or radicals are made use of here in the rational formulas of organic compounds, as $(OH)^I$ hydroxyl, $(NO_2)^I$ the nitro-group, $(NO)^I$ the nitroso-group, $(NH_2)^I$ the amido-group, $(NH)^{II}$ the imido-group, $(N)^{III}$ the nitril-group, $(—N{=}N—)^{II}$ the azo-group, and $(HSO_3)^I$ the sulphonic group.

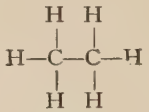
Of the organic radicals, besides methyl, ethyl, propyl, etc., already mentioned, we have the aldehyde group $(CO.H)^I$, the carboxyl group $(COOH)^I$, the ketone group $(CO)^{II}$, and the cyanogen group $(CN)^I$.

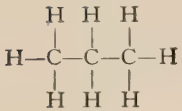
6. Homologous Series.—We have already shown the graphic formulas of methane and ethane, CH_4 and C_2H_6. By continuing the linking of the carbon atoms in the manner there shown we obtain propane, C_3H_8, butane, C_4H_{10}, pentane, C_5H_{12}, and a considerable series of hydrocarbons. It will be noticed that the successive members of this series differ by the constant increment CH_2. Such a series of compounds is called an *homologous* series. Not only may we have an homologous series of hydrocarbons but the homology may extend to the various classes of their derivatives. Thus, we have the homologous series of chlorides $CH_3.Cl$, C_2H_5Cl, C_3H_7Cl, C_4H_9Cl, $C_5H_{11}Cl$, and the homologous series of alcohols CH_3OH, C_2H_5OH, C_3H_7OH, C_4H_9OH, $C_5H_{11}OH$.

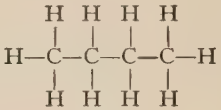
The explanation of this constant increment CH_2 is had when

we write the structural formulas of such a series as just given. Thus, the hydrocarbons before enumerated are:


Methane.


Ethane.


Propane.


Butane.

It will be seen here that in ethane each of the carbon atoms sacrifices one bond to hold together the molecule; that in propane, while each of the end carbon atoms sacrifices one bond, the middle carbon atom must sacrifice two bonds, leaving only two free to attach hydrogen; and in all subsequent members of the series the increase consists simply in inserting additional middle groups CH_2. If we compare such a series to a chain made up of con nected links, we will see that, no matter how much we lengthen the chain, it can have only two end links. The lengthening is in effect but the insertion of more middle links. But in our hydrocarbon chain the middle links are the groups CH_2.

7. Outline of the Classification of Organic Compounds.—In studying the nature, composition, and relationship of organic compounds we soon find that the great majority of them can be arranged in either one or the other of two great classes,—viz., the methane derivatives, sometimes called the fatty bodies, and the benzene derivatives, sometimes called the aromatic compounds. There are, it is true, some compounds which seem to show a transitional character from the one to the other of these groups and some which are not sufficiently understood to allow of their strict classification in this way.

If we take this first division of the subject, the methane derivatives, we have as the groups of compounds to be considered,—

1. Hydrocarbons.—Besides the saturated series already referred to and known specially as the paraffin series, we have unsaturated series of hydrocarbons, such as the olefine and the acetylene series. These are hydrocarbons stable enough to exist temporarily in the free state, but tending to take up either two or four atoms of halogens or monad groups and pass into saturated

compounds. All of these hydrocarbons, however, both saturated and unsaturated, are open-chain hydrocarbons.

2. **Halogen Derivatives of the Hydrocarbons.**—If obtained from the saturated hydrocarbons they are substitution derivatives exclusively ; if formed from unsaturated hydrocarbons they may be addition compounds as well.

3. **Nitro-Derivatives.**—These contain the monad group NO_2, replacing H of the hydrocarbon. They do not form so readily with the methane series of hydrocarbons as with benzene and its homologues.

4. **Alcohols.**—These are hydrates of the hydrocarbon radicals and play the part of weak bases. They may be monatomic, diatomic, etc., according as one, two, or more hydrogen atoms are replaced by the corresponding number of OH groups.

5. **Ethers.**—The oxides of the hydrocarbon radicals, corresponding to the metallic oxides of inorganic chemistry, are termed simple ethers. Two different hydrocarbon radicals may be united by one oxygen atom and so constitute a "mixed ether."

6. **Thio-Ethers and Sulphonic Compounds.**—The first of these classes includes the sulphides of hydrocarbon radicals, the second contains the sulphonic group HSO_3.

7. **Aldehydes and Ketones.**—These classes represent the direct oxidation products of the alcohols. If the alcohol contain the group $CH_2.OH$, that is, belongs to the class of primary alcohols, by oxidation it will yield an aldehyde ; if the alcohol, on the other hand, contain the group CH.OH, that is, belongs to the class of secondary alcohols, by oxidation it will yield a ketone. In the first case, the group $CH_2.OH$ is changed by oxidation into CO.H, the characteristic aldehyde group ; in the second case, the group CH.OH is changed by oxidation into CO, the characteristic ketone group.

8. **Acids.**—When the oxidation of the alcohols or basic hydrates is carried to completion, in the case of primary alcohols (those containing the $CH_2.OH$ group) the aldehyde is changed into the corresponding acid, the characteristic group of which is COOH. Acids are monobasic, dibasic, etc., according to the number of such groups they contain.

9. **Esters.**—These are salts containing an organic radical as base, which is combined with either an inorganic or an organic acid.

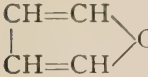
10. Amines and Amides.—Both these classes are ammonia derivatives. If the hydrogen atoms of the ammonia molecule are replaced by a basic radical we have an amine, if by an acid radical an amide.

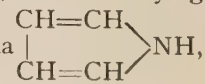
11. Carbohydrates.—These important compounds, known also as the "sugar and starch group," occupy the position of either aldehydes or ketones of hexatomic alcohols, and are treated as a separate group because of convenience and their common origin in the vegetable kingdom.

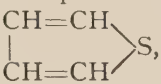
12. Derivatives of Carbonyl.—In these compounds the fundamental group is $(CO)^{II}$, which acts as an acid-forming radical.

13. Derivatives of Cyanogen.—In these compounds the fundamental group is $(CN)^{I}$, which acts in general like the halogen elements.

Intermediate between the open-chain hydrocarbons with their derivatives just enumerated and the closed-chain hydrocarbons of the benzene series (true aromatic compounds) are several groups.

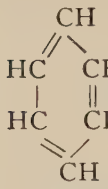
1. Furfuran and its Derivatives.—Furfuran, the starting-point of these compounds, has the structural formula  and shows a closed chain with four carbon atoms.

2. Pyrrol and its Derivatives.—Pyrrol, the underlying compound in this case, has the structural formula  , and also shows a closed chain with four carbon atoms.

3. Thiophen and its Derivatives.—Thiophen, which is found as an accompaniment of benzene in coal-tar, has the structural formula  , showing a closed chain with four carbon atoms.

The aromatic compounds, which, as said, form the second great class of organic substances, are derived from what are termed closed-chain series of hydrocarbons. Six atoms of carbon seem to join together in the closed-chain structure, and this molecule holds together through many reactions. We may also distinguish between aromatic compounds containing one nucleus and those containing more than one nucleus. Under the former class we have,—

1. **Hydrocarbons.**—These may be saturated, unsaturated, or addition hydrocarbons. They all contain the benzene nucleus,



, however, as the central feature of the molecule, and its hydrogen atoms may be replaced by hydrocarbon radicals, as $C_6H_5.CH_3$.

2. **Halogen Derivatives.**—The halogen derivatives of the benzene hydrocarbons may be of two kinds, either with the halogen replacing hydrogen of the nucleus, as $C_6H_4Cl.CH_3$, or hydrogen of the side-group, as $C_6H_5.CH_2Cl$. These two compounds are, it is seen, isomeric.

3. **Sulphonic Derivatives.**—These compounds contain the HSO_3 group replacing hydrogen. They are much more readily formed in the aromatic series than in the methane series and are correspondingly more important.

4. **Nitro-Derivatives.**—Here again the aromatic hydrocarbons are much more readily acted upon than the paraffin series. The action of strong nitric acid easily converts the hydrocarbons and many of their derivatives into the corresponding nitro-derivatives by replacing hydrogen by the group NO_2.

5. **Amido-Derivatives.**—By the action of reducing agents the nitro-derivatives are changed into the corresponding amido-derivatives, the NO_2 group being changed into the NH_2 group. These amido-derivatives, again, give rise to new compounds by the replacement of the hydrogen atoms of the NH_2 group by basic or acid radicals.

6. **Diazo- and Azo-Compounds. Hydrazines.**—Both the diazo- and the azo-compounds contain the dyad group —N=N—. In the former this group is combined on the one side only with a hydrocarbon radical, and in the latter on both sides with hydrocarbon radicals. The aromatic hydrazines are substitution derivatives of hydrazine, NH_2—NH_2.

7. **Phenols and their Derivatives. Quinones.**—The hydroxyl derivatives obtained by replacing by OH the hydrogen in the benzene nucleus of aromatic hydrocarbons are termed phenols. They act like weak acids. We may have monatomic, diatomic, and other phenols according to the number of OH groups so introduced.

The quinones are compounds in which two hydrogen atoms of the benzene nucleus are replaced by a dyad group (O_2).

8. Aromatic Alcohols, Aldehydes, and Ketones.—The aromatic alcohols are isomeric with the phenols, but contain the OH in the side-group, so that they contain the group CH_2OH, and hence are primary alcohols. The aromatic aldehydes are the products of oxidation of these alcohols.

The aromatic ketones, like the ketones of the methane series, contain the dyad group $(CO)^{II}$ linking together two hydrocarbon radicals, of which at least one contains the benzene nucleus.

9. Phenol Alcohols and Phenol Aldehydes.—When both hydrogen of the benzene nucleus and hydrogen of the side-group are replaced by OH groups, we have a phenol alcohol, and this by oxidation of the side-group yields a phenol aldehyde.

10. Aromatic Acids and Phenol Acids.—The product of the full oxidation of the aromatic alcohol is the aromatic acid. It contains the benzene nucleus joined with one or more COOH groups. If the benzene nucleus contain an OH group directly attached in addition, we have the phenol acid.

Under the head of aromatic compounds containing more than one nucleus we have several distinct cases to note.

1. Compounds with Several Uncondensed Nuclei.—We have here included the diphenyl group, the diphenyl-methane and triphenyl-methane groups, and the indigo group.

2. Compounds with Two Condensed Nuclei.—This includes naphthalene and its derivatives.

3. Compounds with Three Condensed Nuclei.—This includes anthracene, phenanthrene, and their derivatives.

4. Compounds containing Nitrogen in the Nucleus.—This includes pyridine, quinoline, and acridine, the first of which corresponds to benzene, the second to naphthalene, and the third to anthracene, with one CH group of the nucleus replaced by nitrogen.

The pharmaceutically and medicinally important classes of *alkaloids* and *ptomaines* follow next. While these compounds have not as yet been sufficiently studied to enable us to classify them in all respects, they appear to be in large part complex derivatives of the bases pyridine and quinoline just referred to.

The classes of *terpenes* and *camphors* are also important as present in the many naturally occurring *essential oils*. With these are also to be considered their products of oxidation, the

resins. Of these several groups are noted, such as oleo-resins, gum-resins, balsams, and hard resins.

The important class of *glucosides* are also considered as supplementary to the regularly classified compounds because of the variety of their composition, as shown by the decomposition products. With them are also noted a number of technically important *dye woods* and other vegetable principles.

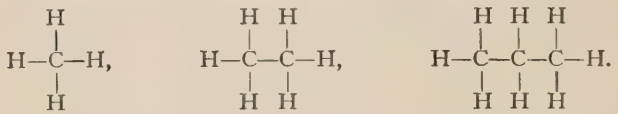
Lastly, the *protein substances* are to be considered, under which head the nature, classification, and reactions of albuminoids will be discussed.

CHAPTER II.

OPEN-CHAIN OR ALIPHATIC HYDROCARBONS.

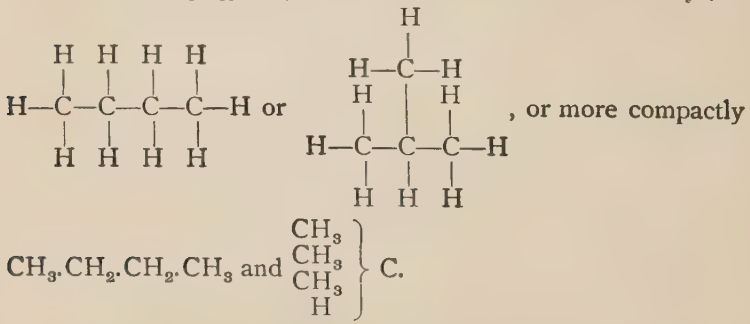
I. The Saturated Hydrocarbons, or Paraffin Series.

1. Composition, Nomenclature, and Molecular Constitution.—We have shown that, while the single atom of tetrad carbon can take up four atoms of hydrogen to form CH_4, two atoms of carbon, when linked together in the same molecule, can take up but six atoms of hydrogen, and three carbon atoms eight atoms of hydrogen. This is shown in the graphic formulas



We have stated under the heading of "Homologous Series" that the difference between any two members of such a series is uniformly CH_2. We are, therefore, able to give a general formula for the entire series, by means of which the formula of any individual hydrocarbon in the series can be deduced. This general formula is C_nH_{2n+2}; that is, for a given number of carbon atoms there will be needed for saturation twice as many hydrogen atoms plus two. More than that number, it is seen from the graphic formulas, cannot be attached.

The first three hydrocarbons of this series, CH_4, C_2H_6, C_3H_8, can only be written structurally as represented above. The next one, however, C_4H_{10}, may be written in either one of two ways,—



$CH_3.CH_2.CH_2.CH_3$ and $\left.\begin{matrix}CH_3\\CH_3\\CH_3\\H\end{matrix}\right\}$ C.

In fact, these different graphic formulas represent two distinct compounds, one boiling at $+1°$ C. and the other at $-17°$ C.,

and known respectively as normal butane and iso-butane, which are isomeric with each other. In the case of C_5H_{12}, three isomeric compounds are possible and have been prepared, and with C_6H_{14} five isomers are possible and are known.

The hydrocarbons of this series have been prepared as far as $C_{35}H_{72}$. They are named by taking the names first applied to the radicals in the case of the first four members of the series, and after that the Greek numerals, and applying the uniform termination *ane*. A table of the hydrocarbons of the paraffin series, with melting and boiling points, is attached.

SATURATED HYDROCARBONS—C_nH_{2n+2}.

Formula.	Name.	Melting Point.	Boiling Point.	
CH_4.	Methane	—186°	—164°	
C_2H_6.	Ethane	. . .	—93°	
C_3H_8.	Propane	. . .	—45°	
C_4H_{10}.	Normal Butane	. . .	+1°	
"	Iso-Butane	. . .	—17°	
C_5H_{12}.	Normal Pentane	. . .	+37°	
"	Iso-Pentane	. . .	+30°	
"	Tertiary Pentane	— 20°	+9°	
C_6H_{14}.	Hexane	. . .	69°	
C_7H_{16}.	Heptane	. . .	98°	
C_8H_{18}.	Octane	. . .	124°	
C_9H_{20}.	Nonane	—51°	150°	
$C_{10}H_{22}$.	Decane	—32°	173°	
$C_{11}H_{24}$.	Undecane	—26°	195°	
$C_{12}H_{26}$.	Dodecane	—12°	214°	
$C_{13}H_{28}$.	Tridecane	—6°	234°	
$C_{14}H_{30}$.	Tetradecane	+5°	253°	
$C_{15}H_{32}$.	Pentadecane	10°	270°	
$C_{16}H_{34}$.	Hexadecane	18°	287°	
$C_{17}H_{36}$.	Heptadecane	22°	303°	
$C_{18}H_{38}$.	Octadecane	28°	317°	
$C_{19}H_{40}$.	Nonadecane	32°	330°	
$C_{20}H_{42}$.	Eicosane	37°	205°	Under a pressure of 15 mm.
$C_{21}H_{44}$.	Heneicosane	40°	215°	
$C_{22}H_{46}$.	Docosane	44°	224°	
$C_{23}H_{48}$.	Tricosane	48°	234°	
$C_{24}H_{50}$.	Tetracosane	51°	243°	
$C_{27}H_{56}$.	Heptacosane	60°	270°	
$C_{31}H_{64}$.	Hentriacontane	68°	302°	
$C_{32}H_{66}$.	Dotriacontane	70°	310°	
$C_{35}H_{72}$.	Pentatriacontane	75°	331°	

2. Occurrence, Preparation, and Description of the More Important.—The hydrocarbons of the paraffin series occur abundantly, ready formed in nature, in various crude petroleums. The

lower members of the series, which are gaseous at ordinary temperatures, also occur as natural gas, which escapes from the earth in many localities; the middle members of the series make up the bulk of the petroleums, and hold dissolved, when first taken from the earth, both the gases and the higher members of the series, which are solids. These latter may occur by themselves also as ozokerite, or natural paraffine.

These hydrocarbons are also formed in the dry distillation of many naturally-occurring substances, such as bituminous coal, shales, wood, and from fish oils when distilled under strong pressure.

The first of the series, *methane*, is also found abundantly in nature as a product of decomposition, and owes its common name, "marsh gas," to such occurrence. Mixed with small quantities of carbon dioxide and nitrogen, it is formed whenever vegetable matter decomposes in the presence of water, as in the bottom of marshes and springs. Its formation here is due to the slow decomposition of the woody fibre under the special conditions of moisture, and probably the presence of micro-organisms, as it is known that cellulose may undergo a fermentative decomposition in their presence, with carbon dioxide and methane as sole products, according to the reaction: $C_6H_{10}O_5 + H_2O = 3CO_2 + 3CH_4$.

Methane also forms by the slow decomposition and change of bituminous coal, and hence is present in abundance in the galleries of coal-mines which are not properly ventilated. When mixed with air it constitutes the dangerous and explosive mixture known as "fire-damp." Under the name of "light carburetted hydrogen" it is known also in the distillation products of these coals. Thus, coal gas, as manufactured for illuminating purposes, contains from 30 to 40 per cent. of methane; "water gas," made by the action of steam on incandescent carbon, contains from 6 to 12 per cent.; while natural gas, now used in large quantities for fuel purposes, contains from 90 to 95 per cent. of methane.

Methane may be artificially formed by a variety of methods:

Thus, carbon monoxide and hydrogen may be made to unite under the influence of electricity: $CO + 3H_2 = CH_4 + H_2O$.

Or a mixture of carbon disulphide vapor and hydrogen sulphide passed over ignited copper will react: $CS_2 + 2H_2S + 8Cu = CH_4 + 4Cu_2S$. It is generally formed (although somewhat contaminated with ethylene and hydrogen) by the heating

of anhydrous sodium acetate and soda-lime, according to the reaction $CH_3COONa + HONa = CH_4 + CO\begin{cases} ONa \\ ONa \end{cases}$, methane and sodium carbonate being in theory the sole products. Chemically pure methane is obtained by the reduction of methyl iodide, CH_3I, in alcoholic solution with copper-coated zinc (Gladstone and Tribe copper-zinc couple).

Methane is a colorless and odorless gas, condensable to a liquid under a pressure of 180 atmospheres at —11° C. It boils at —164° and solidifies at —186°. It burns with a pale, faintly luminous flame, and forms an explosive mixture with air.

Ethane is found in crude petroleum and in natural gas, and may be formed artificially by the action of zinc or sodium upon methyl iodide, as follows:

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\Big|\begin{matrix} I \\ I \end{matrix} + \begin{matrix} Na \\ Na \end{matrix}\Big| = 2NaI + \begin{matrix} CH_3 \\ | \\ CH_3. \end{matrix}$$

It is a colorless and odorless gas, which can be liquefied at +4° by a pressure of 46 atmospheres. It burns with a pale flame.

Propane, normal *butane*, and normal *hexane*, all occur in crude petroleum, the latter two especially being present in gasoline and similar light fractions. Normal *heptane*, in addition to being present in petroleum, occurs in the oil from the *Pinus sabiniana*, or nut-pine, of California, and under the special name of "abietene" is used as a cleansing and solvent benzine.

The hydrocarbons from $C_{16}H_{34}$ on are solid at ordinary temperatures, and make up the bulk of the products known as *petrolatum*. A mixture of these hydrocarbons of still higher fusing point constitutes the commercial product known as *paraffine*.

The name paraffin (from *parum affinis*), first applied to the solid products as obtained from bituminous coals, has been applied to the whole series of hydrocarbons to indicate the stable character of these compounds. They are incapable of combining with halogens or taking up any additional hydrogen, are not affected by any of the strong acids in the cold, and only slightly when heated, and are not easily oxidized by chromic acid or potassium permanganate.

3. **Pharmaceutically Important Products.**—The first of these is **Benzinum,** U. S. P., and is stated to be "a purified distillate from American pretroleum consisting of hydrocarbons, chiefly of the marsh-gas series (C_5H_{12}, C_6H_{14}), and homologous compounds." It is a transparent, colorless liquid, of neutral

reaction, evaporating without residue and leaving no odor, of sp. gr. 0.670 to 0.675 at 15°, and boiling at 50° to 60° C. It is used as a solvent for fats, resins, rubber, and some of the alkaloids.

Petrolatum Liquidum, U. S. P., is stated to be "a mixture of hydrocarbons, chiefly of the marsh-gas series, obtained by distilling off the lighter and more volatile portions from petroleum, and purifying the residue when it has the desired consistence."

Petrolatum Molle, U. S. P., and **Petrolatum Spissum,** U. S. P., are both stated to be "mixtures of hydrocarbons, chiefly of the marsh-gas series, obtained by distilling off the lighter and more volatile portions from petroleum, and purifying the residue when it has the desired melting point." They are manufactured on the large scale under the trade names of vaseline, cosmoline, etc., by the filtration of oil residuums through heated bone-black.

The liquid petrolatum is a colorless or more or less yellowish, oily, transparent liquid, without odor or taste. It has a sp. gr. of 0.875 to 0.945 at 15° C.; the soft petrolatum, on the other hand, is a fat-like mass of about the consistence of an ointment, varying from white to yellowish or yellow, more or less fluorescent when yellow, especially after being melted, completely amorphous, and without odor or taste; and the hard petrolatum is a fat-like mass of about the consistency of a cerate, and in color like the softer variety. The melting point of the soft petrolatum is from 40° to 45° C., and of the hard variety from 45° to 51° C. All these varieties are insoluble in water, scarcely soluble in cold or hot alcohol, or in cold absolute alcohol, but soluble in boiling absolute alcohol, and readily soluble in ether, chloroform, carbon disulphide, oil of turpentine, benzine, benzene, and fixed or volatile oils.

Paraffinum Durum, B. P., is the solid commercial paraffine or paraffine wax, as it is often called. This is a white, waxy, inodorous, tasteless substance, of sp. gr. 0.877, melting (according to its source, whether from petroleum, coal, or ozokerite) between 43° and 65° C.

4. Technically Important Products.—The most important industry based upon the utilization of the hydrocarbons of this series is the refining of petroleum, which, as before stated, is a naturally occurring hydrocarbon mixture. In the United States the most important deposits of petroleum are those of Western Pennsylvania. These oil-fields extend into New York State and into Western Virginia and Ohio. In the latter State (as well as in

the province of Ontario, Canada) is also produced a petroleum of somewhat different character, viz., a sulphur-containing oil, which presents greater difficulties in refining. Petroleum is also found in Kentucky, Colorado, and California, but of a heavier and thicker kind. The most important foreign production is that of Baku, on the Caspian Sea, where enormous quantities of petroleum are obtained. Chemically it differs, however, from the Pennsylvania oil in containing a distinct series of hydrocarbons, the so-called "naphthenes" (see Aromatic Hydrocarbons).

The refining of petroleum consists first in submitting it to a fractional distillation, the products of which are benzine, naphtha, burning oils, and residuum. The latter is then distilled at a higher temperature in separate stills, and yields paraffin oils and a coke or petroleum pitch. All the fractions require a treatment with sulphuric acid, followed by washing and treatment with alkali to remove impurities and products of destructive distillation, which impair their color and burning qualities. The paraffine oils are then chilled by artificial means and paraffine scale separated out from the heavy oils, which then are known as lubricating oils. The paraffine scale when purified by melting, pressing, and filtration yields the white paraffine wax.

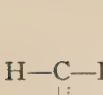
The most important test to be applied to a burning oil is the "fire test," which determines the temperature to which it may be heated without liberating vapors which mixing with air may produce an explosive mixture. The lowest legal test in any of the States is 110° F., and in many it is placed at 150° F.

II. The Unsaturated Hydrocarbons of the Olefine Series.

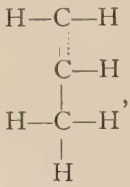
Associated with the paraffin series or saturated hydrocarbons in petroleum, and capable of being formed in most cases of destructive distillation, is a series of hydrocarbons each member of which contains two hydrogen atoms less than the corresponding member of the saturated series. They possess the general formula C_nH_{2n}.

The first member of the series, CH_2, is apparently incapable of existing in the free state, although derivatives of it are known. The second hydrocarbon, C_2H_4, known as ethylene, the third, C_3H_6, known as propylene, and the succeeding ones as high as $C_{30}H_{60}$, are, however, obtainable. The explanation generally accepted by chemists for their molecular structure is that in them two carbon atoms are temporarily doubly linked, but that, as

this double linking is unstable, they act as unsaturated compounds, and readily unite with halogens and atomic groups to form saturated compounds. Thus we have for ethylene



and for propylene



, or, written more compactly, $CH_2{=}CH_2$ and $CH_2{=}CH{-}CH_3$. Their most characteristic reaction is the direct combination with two atoms of the halogens to form *addition compounds*, while the saturated hydrocarbons of the paraffin series can only form *substitution compounds*. Thus, $C_2H_4 + Cl_2 = C_2H_4Cl_2$. They have been named by adding the termination *ene* to the name of the monad radical derived from the corresponding saturated hydrocarbon.

In their physical properties they resemble the methane homologues closely, the first three being gases, C_5H_{10} a volatile liquid, and the higher members being solids like the paraffins.

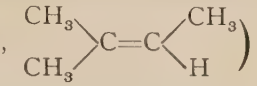
Most of the olefines are easily soluble in alcohol and ether but insoluble in water. Besides their ability to take up halogens to form addition compounds, they are characterized by a tendency to polymerize, especially in the presence of sulphuric acid or zinc chloride, and by the readiness with which they are oxidized by chromic acid or potassium permanganate.

They are formed together with the paraffins by the destructive distillation of many substances, such as fats, waxes, lignite, and coal; illuminating gas consequently contains the olefines, and upon them in fact mainly depends its illuminating value.

Ethylene, C_2H_4, is present to the extent of from 5 to 6 per cent. in illuminating gas made from coal, but it is usually prepared by the action of an excess of strong sulphuric acid upon alcohol, the reaction being simply a dehydration of the alcohol: $C_2H_6O - H_2O = C_2H_4$.

It is a colorless gas, which may be liquefied at 0° C. by a pressure of 44 atmospheres. It is very slightly soluble in water and alcohol and burns with a luminous flame. It unites directly with an equal volume of chlorine to form ethylene dichloride, which condenses to oily drops, whence the name often given of "olefiant" (or oil-forming) gas. It combines with two atoms of hydrogen in the presence of spongy platinum to form ethane, C_2H_6.

Propylene and the several isomeric *butylenes* have been prepared.

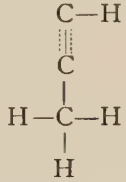
Of the *amylenes*, one (trimethyl-ethylene, ) has been introduced into medicine as an anæsthetic under the name of "pental." It is formed from tertiary amyl alcohol (amylene hydrate) by the action of dehydrating agents. It is a colorless, mobile, very volatile, and inflammable liquid, boiling at 37°–38° C. It is insoluble in water, but miscible in all proportions in chloroform, ether, and 90 per cent. alcohol.

Isomeric with the olefines are certain closed-chain hydrocarbons, such as *trimethylene*, C_3H_6, and *hexamethylene*, C_6H_{12}. These will be referred to later under closed-chain hydrocarbons (see p. 741).

III. The Unsaturated Hydrocarbons of the Acetylene Series.

A third series of hydrocarbons, containing two hydrogen atoms less than the corresponding members of the olefine series and four less than the members of the paraffin series, is known under the name of the acetylene series. They have, therefore, the general formula C_nH_{2n-2}.

To explain their unsaturated character and their ability to take up four atoms of halogen or other atom or group, we assume the following structural formula for acetylene, or $CH{\equiv}CH$

and for the second member, allylene,  or $CH{\equiv}C{-}CH_3$.

The first five members of this series are

Acetylene, C_2H_2,
Allylene, C_3H_4,
Crotonylene or Butine, C_4H_6,
Valerylene or Pentine, C_5H_8,
Hexine, C_6H_{10}.

They are produced in the destructive distillation of many organic compounds, such as wood and bituminous coal. Acetylene, the first member of the series, is produced in a variety of additional ways. Thus, when methane, ethane, ethylene, alcohol, ether, and aldehyde are led through tubes heated to redness, acetylene is produced with separation of hydrogen and other prod-

ucts. The incomplete combustion of many carbon compounds also causes the formation of acetylene, as in the case of defective gas-burners and in the use of gas-stoves. The simplest reaction for its production is the passage of the electric spark between carbon points in an atmosphere of hydrogen. We have here a direct organic synthesis, and from the acetylene so formed many other complex organic compounds can be built up. Acetylene, however, is most abundantly formed by the decomposition of metallic carbides in the presence of water. Since the development of the electric furnace by Moissan and others the manufacture of carbides, such as calcium carbide, CaC_2, has assumed great importance because of the convenience with which they may be made to yield acetylene.

Acetylene is a colorless gas with a peculiar penetrating odor, recognizable in cases of defective combustion with gas-burners. It burns from an ordinary burner with a rich, luminous, but sooty flame; from specially constructed burners with very narrow openings it can be made, on the other hand, to burn with a very pure, intense, whitish light. It forms explosive compounds with potassium, sodium, silver, and copper, in which one or both hydrogen atoms are replaced by metal. It is capable of uniting with hydrogen when a mixture of the two is passed over heated platinum black, four atoms being taken up and ethane being formed.

IV. Unsaturated Hydrocarbons of the Series C_nH_{2n-4} and C_nH_{2n-6}.

In the distillation products of cannel coal, as well as in bone oil (Dippel's oil), are contained hydrocarbons of the series C_nH_{2n-4}. These are unsaturated, and take up six atoms of bromine by addition to form saturated compounds. They precipitate ammoniacal silver and copper solutions like acetylene.

Two hydrocarbons of this character have been described, *valylene*, C_5H_6, and *diallylene*, C_6H_8.

The terpenes, $C_{10}H_{16}$, which would answer to the general formula C_nH_{2n-4}, do not belong here, as they seem to be addition products of the aromatic compounds.

The only well-defined representative of the series C_nH_{2n-6} is *dipropargyl*, C_6H_6. This compound, isomeric with the aromatic hydrocarbon benzene, is an unsaturated open-chain hydrocarbon, as is shown by the readiness with which it adds on bromine and precipitates ammoniacal silver and copper salts.

CHAPTER III.

DERIVATIVES OF THE OPEN-CHAIN HYDROCARBONS.

I. Halogen Derivatives.

1. Substitution Derivatives of the Paraffin Series.—Chlorine and bromine are capable of acting directly upon the hydrocarbons, replacing hydrogen. This action is facilitated by the presence of sunlight or substances which act as the "carriers" of the chlorine and bromine, such as iodine, ferric chloride, or antimony chloride. Iodine does not act directly upon the hydrocarbons, so that the iodides are generally obtained by the action of HI upon the several alcohols (see under Alcohols.)

TABULAR VIEW OF THE HALOID DERIVATIVES OF THE PARAFFINS.

	Boiling Point
Mono-Derivatives:	
Monochlor-methane, or Methyl chloride, CH_3Cl	—22° C.
Methyl bromide, CH_3Br	+4°
Methyl iodide, CH_3I	44°
Monochlor-ethane, or Ethyl chloride, C_2H_5Cl	12°
Ethyl bromide, C_2H_5Br	39°
Ethyl iodide, C_2H_5I	72°
Propyl iodide, Isopropyl iodide, C_3H_7I	102°
Four isomeric varieties of Butyl iodide, C_4H_9I.	
Iso-amyl chloride, $C_5H_{11}Cl$	101°
Hexyl chloride, $C_6H_{13}Cl$	126°
Di-Derivatives:	
Dichlor-methane, or Methylene chloride, CH_2Cl_2	42°
Methylene bromide, CH_2Br_2	97°
Methylene iodide, CH_2I_2	180°
Ethylene chloride, } $C_2H_4Cl_2$	84°
Ethylidene chloride, } $C_2H_4Cl_2$	57°
Tri-Derivatives:	
Trichlor-methane, or Chloroform, $CHCl_3$	61°
Bromoform, $CHBr_3$	151°
	Melting Point
Iodoform, CHI_3	119°
Higher Substitution Products:	
Tetrachlor-methane, or Carbon tetrachloride, CCl_4	77°
Perchlor-ethane, C_2Cl_6	185°

Besides the direct substituting action of chlorine and bromine upon the hydrocarbons, we can use the action of the haloid acids, HCl, HBr, and HI, upon the corresponding alcohol, as shown in the reaction $C_2H_5.OH + HBr = C_2H_5Br + H_2O$, or the direct addition of these haloid acids to the olefine hydrocarbons according to the reaction $C_2H_4 + HCl = C_2H_5Cl$.

The halogen substitution products of these hydrocarbons are almost if not quite insoluble in water, but miscible to any extent with alcohol and ether. The lower ones in the series possess in general a sweet ethereal odor and produce insensibility and unconsciousness when inhaled.

Methyl Chloride, CH_3Cl, is prepared by heating methyl alcohol with a mixture of salt and sulphuric acid, or direct with dry hydrochloric acid gas in the presence of fused chloride of zinc. It forms a colorless gas with ethereal odor, burning with green-edged flame. Under a pressure of 5 atmospheres it is liquefied, and this liquefied gas is now largely used as a means of artificial refrigeration and for local anæsthetic effect in surgery. A saturated solution of methyl chloride in chloroform constitutes the "compound liquid" used as an anæsthetic by Richardson. Methyl chloride is also made as a technical product by distilling the "vinasse" of the beet-sugar factories and heating the trimethylamine hydrochlorate obtained to 360° with hydrochloric acid. As so obtained it is used in the aniline dye color industry.

Methyl Iodide, CH_3I, is prepared from methyl alcohol, phosphorus, and iodine. It forms a colorless liquid, boiling at 44°, and is used in the manufacture of organic dye colors.

Ethyl Chloride, C_2H_5Cl, is a colorless mobile liquid, boiling at 12°, only slightly soluble in water, but easily soluble in alcohol, which latter solution is sometimes known as solution of "chloric ether." Used somewhat as a local anæsthetic.

Ethyl Bromide, C_2H_5Br, is best prepared by the action of a mixture of sulphuric acid and alcohol upon potassium bromide followed by distillation. The distillate is shaken up with potassium carbonate to free it from hydrogen bromide, and then dehydrated with calcium chloride and again distilled. It forms a colorless mobile liquid, of sweet chloroform-like odor and burning taste, boiling at 38°–39°. It is insoluble in water, but miscible with alcohol, ether, chloroform, fatty and ethereal oils. As it is decomposed gradually by the influence of the air and light, it must be preserved in dark bottles. It has been repeatedly recommended and tried as an anæsthetic, but has not found gen-

eral acceptance, perhaps because of its tendency to decompose, with production of free bromine and hydrogen bromide.

Methylene Chloride, CH_2Cl_2, can be prepared by the action of chlorine upon methane or methyl chloride, or by the action of nascent hydrogen upon chloroform. It forms a colorless liquid with chloroform-like odor, boiling at 42°. It has been found to possess properties very similar to chloroform, producing an anæsthetic effect slightly more transient in character. This pure methylene chloride must not be confounded with a preparation brought out under the same name in England, which has been shown to be a mixture of 1 volume methyl alcohol and 4 volumes of chloroform.

Ethylene Chloride, $C_2H_4Cl_2$, is one of two isomeric compounds. It possesses the structural formula $CH_2Cl.CH_2Cl$, while its isomer, ethylidene chloride, has the formula $CH_3.CHCl_2$. Ethylene chloride is sometimes known as the "oil of the Dutch chemists," or simply as "Dutch liquid," because the reaction whereby it was formed by the direct union of ethylene and chlorine gases was first discovered in Amsterdam. It is a colorless liquid, of chloroform-like odor and sweet taste, and has been used as a substitute for chloroform both for external applications and for inhalations.

Ethylidene Chloride, $C_2H_4Cl_2$, is obtained as a by-product in the manufacture of chloral, or can be prepared by the action of phosphoric chloride upon paraldehyde. It is a colorless liquid, smelling like chloroform and of a sweet taste. It has been proposed by Liebreich as a substitute for chloroform in cases of anæsthesia.

Trichlor-methane, or **Chloroform**, U. S. P., $CHCl_3$, was discovered independently by Liebig and Soubeiran in 1831. Besides the preparation from methane by the action of chlorine, which is purely a theoretical process, we have three practical methods for its preparation.

(*a*) From alcohol by the action of chlorinated lime. This reaction most probably takes place in several stages. The chlorinated lime first oxidizes the alcohol to aldehyde according to the reaction :

$$C_2H_6O + CaOCl_2 = CaCl_2 + C_2H_4O + H_2O.$$

The aldehyde is then changed by the chlorinated lime into trichloraldehyde :

$$2C_2H_4O + 6(CaOCl_2) = 3CaCl_2 + 3Ca(OH)_2 + 2C_2HCl_3O.$$

The chloral thus formed is then decomposed by the alkaline calcium hydrate :

$$2C_2HCl_3O + Ca(OH)_2 = Ca(CHO_2)_2 + 2CHCl_3,$$

the end products being chloroform and calcium formate.

(*b*) From acetone by the action of chlorinated lime. This reaction, already pointed out by Liebig in 1832, has been taken up in recent years, and is now largely used in the manufacture of chloroform. It is as follows :

$$2C_3H_6O + 6CaOCl_2 = 2CHCl_3 + 2Ca(OH)_2 + Ca(C_2H_3O_2)_2 + 3CaCl_2.$$

(*c*) From chloral by the action of caustic alkalies, the reaction being analogous to that given under the first process.

Chloroform is a heavy, colorless, mobile, and diffusible liquid, of ethereal odor and burning, sweet taste. Specific gravity 1.49 at 15°. It boils at 60° to 61°. Chloroform is an excellent solvent for phosphorus, iodine, alkaloids, resins, caoutchouc, fats, fatty oils, etc. When exposed to the light it is liable to decomposition with liberation of hydrochloric acid and free chlorine, and hence must be kept in dark bottles. Its preserving qualities are improved by the addition of a small quantity of alcohol.

The most delicate chemical test for chloroform is the production of phenylcarbylamine, a compound of sickening odor when it is heated with alcoholic potash and aniline. One part of chloroform in 5000 to 6000 parts of solution can be detected in this way.

The most important medicinal use of chloroform is as an anæsthetic.

Tribromo-methane, or bromoform, $CHBr_3$, can be prepared from bromal by an analogous reaction to that used for preparing chloroform from chloral. It is a colorless liquid smelling like chloroform, and is somewhat used in medicine as an anæsthetic.

Triiodo-methane, or **Iodoform**, U. S. P., CHI_3, has been made most generally by the action of iodine in the presence of an alkali or alkaline carbonate upon alcohol, the main reaction being expressed as follows :

$$C_2H_5OH + 4I_2 + 3K_2CO_3 = CHI_3 + KCHO_2 + 5KI + 2H_2O + 3CO_2.$$

It is also made now by the action of iodine in the presence of an alkali upon acetone, the reaction being a very delicate one, serving to indicate traces of acetone, and known as the "iodoform test."

Iodoform is in small, lemon-yellow, lustrous crystals of the hexagonal system, with a peculiar, very penetrating and persistent odor, resembling saffron. The crystals melt at 119° C. They are very slightly soluble in water, soluble in alcohol, ether, chloroform, benzine, and fixed and volatile oils. It has a strong anæsthetic and antiseptic action, and is much used in surgery.

Tetrachlor-methane, or carbon tetrachloride, CCl_4, is a liquid boiling at 76.5° C.

Perchlor-ethane, C_2Cl_6, forms rhombic tablets of camphor-like odor. Fuse and boil at 185°.

2. **Halogen Derivatives of the Olefine Series.**—These may be either substitution derivatives, in which one or more H atoms of the unsaturated hydrocarbon are replaced by halogen, the double linking of carbon atoms characteristic of the olefines remaining unchanged, or they may be addition compounds, in which case two atoms of halogen add on. In the compounds so formed the unstable double linking is broken up, and the product is in all respects identical with the dihalogen substitution derivatives of the paraffins. Thus, from ethylene, C_2H_4, we may obtain C_2H_3Cl, monochlor-ethylene (vinyl chloride), and $C_2H_2Cl_2$, dichlor-ethylene, or we may get by addition $C_2H_4Cl_2$, ethylene chloride, already described under the preceding class. From propylene, C_3H_6, we may obtain C_3H_5Cl, monochlor-propylene (allyl chloride), representing the substitution derivatives, or $C_3H_6Cl_2$, propylene chloride, representing the addition compounds.

3. **Halogen Derivatives of the Acetylene Series.**—Here also both classes of compounds are possible,—substitution derivatives, in which the unstable treble linking still remains, and addition compounds, which pass into the class of olefine derivatives.

II. Alcohols, or Hydrates of the Hydrocarbon Radicals.

Alcohols are formed by the replacement of one or more hydrogen atoms of a hydrocarbon by the corresponding number of OH (hydroxyl) groups.

Alcohols with 1 hydroxyl group are termed *monatomic*, or monacid; alcohols with 2 hydroxyl groups are termed *diatomic*, or diacid; alcohols with 3 hydroxyl groups are termed *triatomic*, or triacid.

The highest of these classes as yet discovered in nature are the heptatomic alcohols, although higher ones have been obtained

artificially. Two cases of isomerism may arise among the alcohols : (*a*) when they are derived from isomeric hydrocarbons ; thus, from butane, $CH_3.CH_2.CH_2.CH_3$, we obtain normal butyl alcohol, $CH_3.CH_2.CH_2.CH_2OH$, and from isobutane, $\begin{matrix}CH_3\\CH_3\end{matrix}>CH—CH_3$, we obtain isobutyl alcohol, $\begin{matrix}CH_3\\CH_3\end{matrix}>CH—CH_2OH$; (*b*) according to the position taken by the replacing hydroxyl group ; thus, while only one monatomic alcohol can be formed from methane, CH_4, and only one from ethane, $CH_3.CH_3$, from propane, $CH_3.CH_2.CH_3$, we can obtain normal propyl alcohol, $CH_3.CH_2.CH_2OH$, and isopropyl alcohol, $CH_3.CH.OH.CH_3$. Normal butane yields two isomeric alcohols, $CH_3.CH_2.CH_2.CH_2OH$ and $CH_3.CH_2.CH.OH.CH_3$, and isobutane yields two also, $\begin{matrix}CH_3\\CH_3\end{matrix}>CH—CH_2OH$ and $\begin{matrix}CH_3\\CH_3\end{matrix}>C(OH)—CH_3$.

In looking at the formulas of these isomeric butyl alcohols it will be seen that we have three different types of monatomic alcohols : an alcohol containing the group $CH_2.OH$, known as a *primary* alcohol ; an alcohol containing the group CH.OH, known as a *secondary* alcohol ; an alcohol containing the group C(OH), known as a *tertiary* alcohol. We will find that these are important distinctions, as very different products are obtainable from the alcohols according as they belong to one or the other of these classes.

Secondary and tertiary alcohols are also known as *carbinols*, and the groups combined with the carbon atoms to which the hydroxyl is attached are specially named.

Thus, $\begin{matrix}CH_3\\CH_3\end{matrix}>C(OH)—CH_3$ is called trimethyl-carbinol.

1. Monatomic Alcohols from Saturated Hydrocarbons. General formula, $C_nH_{2n+1}.OH$.

TABLE.

Name and Formula :	Boiling Point.
Methyl alcohol, $CH_3.OH$	66° C.
Ethyl alcohol, $CH_3.CH_2OH$	78°
Normal propyl alcohol, $CH_3.CH_2.CH_2OH$	97°
Isopropyl alcohol, $CH_3.CHOH.CH_3$	83°
Normal butyl alcohol, $CH_3.CH_2.CH_2.CH_2OH$	117°
Isobutyl alcohol, $\begin{matrix}CH_3\\CH_3\end{matrix}>CH.CH_2OH$	108°
Methyl-ethyl carbinol, $\begin{matrix}CH_3.CH_2\\CH_3\end{matrix}>CHOH$	99°

TABLE.—*Continued.*

Name and Formula:	Boiling Point.
Trimethyl carbinol, $\frac{CH_3}{CH_3}>C(OH).CH_3$	83°
Normal amyl alcohol, $C_4H_9.CH_2OH$	137°
Fermentation amyl alcohol, $\frac{CH_3}{CH_3}>CH.CH_2.CH_2OH$	131°
Hexyl alcohol, $C_6H_{13}.OH$	157°
Heptyl alcohol, $C_7H_{15}.OH$	175°
Octyl alcohol, $C_8H_{17}.OH$	191°
Nonyl alcohol, $C_9H_{19}.OH$	213°
	Melting Point.
Decyl alcohol, $C_{10}H_{21}.OH$	7°
Dodecyl alcohol, $C_{12}H_{25}.OH$	24°
Tetradecyl alcohol, $C_{14}H_{29}.OH$	38°
Hexadecyl (cetyl) alcohol, $C_{16}H_{33}.OH$	49°
Octadecyl alcohol, $C_{18}H_{37}.OH$	59°
Ceryl alcohol, $C_{27}H_{55}OH$	79°
Myricyl alcohol, $C_{30}H_{61}.OH$	85°

The lower members of the series are mobile liquids soluble in water, the middle members are oily liquids only slightly soluble in water, and the higher ones are solid crystalline bodies. The lowest members possess an alcoholic odor, those over C_5 an odor of fusel oil, and both have a burning taste, while the highest members are odorless and tasteless solids.

Among the general methods for the formation of alcohols may be mentioned:

(*a*) The action of moist silver oxide upon the halogen derivatives of the paraffins, as $C_2H_5I + AgOH = C_2H_5.OH + AgI$.

(*b*) The decomposition of the esters by boiling with caustic alkalies. This decomposition is frequently spoken of as the "saponification" of the esters, because of the well-known illustration of the decomposition of the fats:

$$\underset{\text{Methyl Salicylate.}}{CH_3.OC_7H_5O_2} + KOH = CH_3.OH + \underset{\text{Potassium Salicylate.}}{C_7H_5O_2.OK}.$$

(*c*) The treatment of primary amines with nitrous acid:

$$C_2H_5.NH_2 + NO.OH = C_2H_5.OH + N_2 + H_2O.$$

(*d*) The fermentation of many of the carbohydrates (as grape sugar) with yeast will produce the lower alcohols. (See Fermentation.)

Among the special methods for the formation of alcohols may be mentioned :

(*a*) The reduction of monobasic acids and aldehydes with nascent hydrogen to form primary alcohols.

(*b*) The reduction of ketones with nascent hydrogen to form secondary alcohols.

The alcohols, it must be remembered, are hydrates of radicals which have in general a basic character. They are, therefore, weak bases. Thus, the hydrogen of the hydroxyl group is replaceable by acid radicals, forming ethereal salts or "esters." At the same time, this hydrogen is also replaceable by strong metals like Na and K, forming "alcoholates." The action of haloid acids will also replace the OH group by halogen, water forming at the same time. Thus, $C_2H_5.OH + HBr = C_2H_5Br + H_2O$. Oxidizing agents readily act upon them, changing primary alcohols to aldehydes and monobasic acids, and secondary alcohols to ketones, while tertiary alcohols are split up into compounds with a lesser number of carbon atoms.

Methyl Alcohol, $CH_3.OH$, derives its name from μέθυ, wine, and ὕλη, wood, which idea is also conveyed in its popular name of "wood-spirit." It occurs as salicylic ester in *Gaultheria procumbens* (oil of wintergreen), and is produced in the destructive distillation of wood and the "vinasse" of the beet-sugar refineries.

To prepare it in quantity, the crude pyroligneous acid of the wood distilleries is neutralized with lime, and the volatile portions then distilled off. After repeated rectification, the methyl alcohol is finally freed from acetone and accompanying impurities by forming the crystalline oxalic ester, which is pressed, dried, and decomposed by boiling with water or ammonia.

Methyl alcohol forms a colorless liquid, boiling at 66°, and with a sp. gr. 0.8. It burns with a non-luminous flame, and mixes with water in all proportions. It is a solvent for fatty oils, camphors, resins, and fats. It has an intoxicating effect, and in concentrated form is poisonous.

Ethyl Alcohol, $C_2H_5.OH$ (**Alcohol,** U.S.P.).—This, the most important of the monatomic alcohols, occurs only sparingly in nature, being found as butyric ether in some plants, as the Umbellifera, and in the animal kingdom, as in diabetic urine. It may be formed in several ways :

From ethane by conversion into C_2H_5Cl, and saponification of this latter (see preceding page) by moist silver oxide.

From ethylene and concentrated sulphuric acid and decomposition of the resulting ethyl-sulphuric acid by water :

$$C_2H_4 + SO_2(OH)_2 = C_2H_5.HSO_4.$$
$$C_2H_5.HSO_4 + H_2O = C_2H_5OH + H_2SO_4.$$

It is formed, however, almost invariably by the "alcoholic fermentation" of sugar. (See Fermentation.) The reaction whereby the sugar yields alcohol and carbon dioxide, $C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$, is not a complete one, as some 5 per cent. of the sugar breaks up into other products, such as glycerin and succinic acid. A number of the homologues of ethyl alcohol are also formed, and are known collectively as "fusel oil."

While alcohol may be purified by repeated distillation, it is not possible to free it from water by this means. On a large scale in the several forms of rectifying columns it is possible to bring the alcohol to 98–99 per cent., but on the small scale to not over 95 per cent. The remaining portion of water must be taken out by chemical dehydrating agents, like heated carbonate of potash, anhydrous sulphate of copper, or standing, followed by a distillation over quick-lime. The alcohol thus obtained is the **Alcohol Absolutum,** U. S. P.

The presence of water in alcohol may be shown by admixture with benzene. This will mix to a clear liquid with alcohol containing not more than 3 per cent. of water. If the percentage begins to exceed this, the mixture becomes turbid. Anhydrous copper sulphate will also indicate the presence of water by changing from white to blue in color. Absolute alcohol boils at 78.5° C., becomes viscid at —100° C., and solidifies at —130°. Its specific gravity is 0.7937 at 15° C. It is very hygroscopic. Alcohol is a solvent for many organic compounds, such as fats, resins, and oils.

A very delicate test for alcohol (although not characteristic of alcohol only) is the iodoform test. The liquid to be tested is warmed with a small quantity of iodine dissolved in iodide of potassium solution, and sodium hydrate is added until the mixture is faintly yellow. In the presence of alcohol the characteristic smell of iodoform is obtained, and gradually the fine yellow crystals separate.

Benzoyl chloride, C_6H_5COCl, is also a delicate test for alcohol, with which it forms ethyl benzoate (benzoic ether), the smell of which is readily recognized. The commonest impurities of alcohol are aldehyde, which readily forms by oxidation, and fusel oil,

which accompanies it in the products of fermentation. The former is detected by shaking up with a small quantity of potassium hydrate solution, whereby a brown aldehyde resin is formed ; the latter is detected by evaporation of the suspected alcohol on the hand or from a piece of blotting-paper.

Besides alcohol (containing 94 per cent. by volume of ethyl alcohol) and alcohol absolutum, the United States Pharmacopœia recognizes **Alcohol Deodoratum** and **Alcohol Dilutum,** the latter containing about 48.6 per cent. by volume of absolute ethyl alcohol.

Alcohol has a dehydrating action upon vegetable and animal tissues. It coagulates albumen and prevents the decay of the tissue. Taken in small amount it has a slight stimulant effect ; in larger doses it lowers the temperature and acts as an intoxicant, while in excessive amounts it is poisonous, and when injected into the veins it causes death. A portion of the alcohol taken into the system is burned to carbon dioxide and water ; the remainder passes off through the lungs and the urine unchanged.

For an account of alcoholic beverages, see Fermentation Industries.

Propyl Alcohols, C_3H_7OH.—The normal propyl alcohol, $CH_3.CH_2.CH_2OH$, is contained in fusel oil, from which it may be obtained by fractionation. It may also be obtained by the action of sodium amalgam upon propion-aldehyde, or by the action of certain fissure ferments upon glycerin.

It is a liquid of spirituous odor, resembling that of methyl alcohol, boiling at 97.4°, and readily miscible with water, but can be separated out again by addition of calcium chloride. Isopropyl, or secondary propyl alcohol, $CH_3.CH(OH).CH_3$, may be obtained from isopropyl iodide (the product of the action of HI upon glycerin), or by the action of sodium amalgam upon acetone. Colorless liquid, boiling at 82.8°.

Butyl Alcohols, $C_4H_9.OH$.—The normal butyl alcohol, $CH_3.CH_2.CH_2.CH_2OH$, is present in fusel oil, being formed especially in the wine-yeast fermentation. It is also formed readily from glycerin by the fermentation with fissure ferments. It boils at 117°, and has a peculiar odor, inciting to coughing when inhaled. It is not so readily soluble in water, and may readily be separated out on addition of calcium chloride. Isobutyl alcohol, $\begin{matrix}CH_3\\CH_3\end{matrix}>CH.CH_2OH$, known frequently as fermentation butyl alcohol, is the most important of the butyl alcohols. It is contained

in fusel oil, especially in potato fusel oil, and obtained in the beer-yeast fermentation. Colorless liquid, boiling at 108°, with a fusel smell, resembling that of wild jasmine.

Tertiary butyl alcohol, or trimethyl carbinol, $(CH_3)_3{=}C(OH)$, is contained in small quantity in fusel oil. Spirituous smell resembling that of camphor. The remaining butyl alcohol, known as secondary butyl alcohol (see table), is only obtained synthetically.

Amyl Alcohols, $C_5H_{11}.OH$.—Of the eight possible isomeric alcohols, only four require mention. Normal primary amyl alcohol is contained in small quantity in fusel oil, and can be prepared by the reduction of normal valeric aldehyde. Its boiling point is 137°. Isobutyl carbinol, $(CH_3)_2{=}CH.CH_2.CH_2OH$, forms the chief constituent of fermentation amyl alcohol obtained from potato fusel oil. Is also found in Roman chamomile oil in combination with angelic and tiglic acids. It boils at 131°, and has a strong, irritating odor. It is intoxicating even in dilute solutions, and is the cause of the peculiar toxic after-effects of intoxication by brandy and other ardent spirits. It is optically inactive. Methyl-propyl carbinol, or active amyl alcohol, is also contained in fermentation amyl alcohol. It turns the plane of polarization to the left. Boiling point, 112.5°. Tertiary amyl alcohol, or dimethyl-ethyl carbinol, $\begin{matrix}(CH_3)_2{=}C(OH),\\ C_2H_5\end{matrix}$ has been introduced to medicine in recent years under the name of "amylene-hydrate," and recommended as an hypnotic. It is made from amylene, C_5H_{10} (see p. 617), by shaking this up with sulphuric acid, whereby amyl sulphuric acid, $SO_2\begin{cases}OH\\ O(C_5H_{11}),\end{cases}$ is formed. This, on distillation with aqueous alkalies, is decomposed into amylene hydrate and alkaline sulphate. The amylene hydrate is a colorless, oily liquid, of penetrating odor, which recalls camphor, peppermint, and paraldehyde. It boils at 102.5°, and has a specific gravity of 0.812 at 12°. It is soluble in 8 parts of water, and miscible in all proportions with alcohol, ether, chloroform, benzine, glycerin, and fatty oils. It is sensitive to light and very hygroscopic. As an hypnotic, it is said to occupy a position intermediate between chloral hydrate and paraldehyde.

Hexyl Alcohols, $C_6H_{13}.OH$.—The normal primary hexyl alcohol is contained as a butyric ester in the seeds of *Heracleum giganteum*. A primary hexyl alcohol is also obtained from wine fusel oil, and a secondary alcohol from mannite through the intermediate formation of secondary hexyl iodide.

Heptyl Alcohols, $C_7H_{15}.OH$.—The normal primary heptyl alcohol is obtained by the reduction of œnanthol, a normal aldehyde which forms on the distillation of castor oil.

Octyl Alcohol, $C_8H_{17}.OH$.—The normal primary octyl alcohol is found as an acetic ester in the several varieties of *heracleum*.

The normal primary alcohols, $C_{10}H_{21}.OH$, $C_{12}H_{25}.OH$, $C_{14}H_{29}.OH$, $C_{16}H_{33}.OH$, and $C_{18}H_{37}.OH$, were prepared artificially by Krafft, in 1881, by reducing the corresponding acids with zinc-dust and acetic acid. They are solids, like paraffin in appearance.

Cetyl Alcohol, $C_{16}H_{33}.OH$, formerly known as *ethal*, is found in combination with palmitic acid as the chief constituent of spermaceti (**Cetaceum**, U. S. P.). The alcohol crystallizes in small leaflets, fusing at 49° and boiling at 189.5°.

Octadecyl Alcohol, $C_{18}H_{37}.OH$, is also found in the form of esters in spermaceti.

Ceryl Alcohol, $C_{27}H_{55}.OH$, is found as cerotic ester in Chinese wax, and as palmitic ester in the ripe capsules of the poppy. The ceryl esters are also present in carnauba wax and in beeswax. The alcohol fuses at 76°–79°.

Myricyl Alcohol, $C_{30}H_{61}.OH$, is present as palmitic ester in beeswax and in carnauba wax, from which latter it is most conveniently extracted by saponification with alcoholic potash. The alcohol melts at 85° C.

2. Monatomic Alcohols from Unsaturated Hydrocarbons, $C_nH_{2n-1}.OH$.—These alcohols are derivatives of the olefine hydrocarbons, and, like them, contain the unstable double linking of two carbon atoms. They, therefore, like them, can take up two atoms of hydrogen or halogen element or one molecule of a haloid acid, forming thereby saturated alcohols, which may contain one or two replacing halogen atoms in the radical which is combined with the hydroxyl.

Vinyl Alcohol, $CH_2{=}CH.OH$, corresponding to Ethylene, $CH_2{=}CH_2$, has been found as an impurity in ordinary ether, but has not been isolated, as the isomeric acetaldehyde, $CH_3.CHO$, results in endeavoring to prepare it.

Allyl Alcohol, $CH_2{=}CH{-}CH_2OH$, corresponding to propylene, C_3H_6, is found in crude wood-spirit, and may be readily obtained by distilling glycerin with oxalic acid, the reaction being $C_3H_8O_3 - H_2O - O = C_3H_6O$, showing that the oxalic acid acts as a reducing and dehydrating agent. It is a mobile, colorless

liquid, of penetrating, unpleasant odor, boiling at 96.6°, and miscible with water.

3. Other Monatomic Alcohols from Unsaturated Hydrocarbons.—The alcohols, $C_nH_{2n-3}OH$, are derivatives of acetylene and its homologues, and, like them, contain the unstable treble linking of two carbon atoms.

Propargyl Alcohol, $CH{\equiv}C{-}CH_2OH$, corresponding to allylene, C_3H_4, is obtained from monobromallyl alcohol by splitting off HBr, effected by the action of concentrated aqueous potash. It is a mobile, pleasant-smelling liquid, lighter than water, boiling at 114°.

Cholesterin, $C_{26}H_{44}O$, is a monatomic alcohol which occurs in combination with various fatty acids in lanolin, the fat of sheep's wool.

4. Diatomic Alcohols or Glycols. General formula, $C_nH_{2n}(OH)_2$.—If two hydrogen atoms of a hydrocarbon of the paraffin series be replaced by two OH groups, we obtain a diatomic alcohol or glycol (from γλυκύς, sweet). Thus, from ethane, C_2H_6, we obtain ethylene glycol, $C_2H_4(OH)_2$. The two OH groups do not, however, attach to the same carbon atoms, so that, while theoretically both ethylidene glycol, $CH_3.CH(OH)_2$, and ethylene glycol, $CH_2OH{-}CH_2OH$, are possible, only the latter can be obtained. For this reason, also, the first of the series of glycols, methylene glycol, $CH_2(OH)_2$, cannot be obtained in the free state, although ethers corresponding to it are known. (See Methylal, p. 646.)

The distinction already noted under monatomic alcohols, of primary, secondary, and tertiary alcohols, of course exists here also, only, instead of three cases, six may arise, from the fact that there are the two replacing OH groups, the position of which is to be considered.

Glycols are formed most readily by forming first the dibromides of the hydrocarbons and then replacing the bromine atoms by hydroxyl groups. This can be effected by boiling the dibromides with water to which potassium carbonate or lead hydrate has been added to take up the hydrogen bromide liberated, the reaction being :

$$\begin{matrix} CH_2{\cdot}Br \\ | \\ CH_2{\cdot}Br \end{matrix} + \begin{matrix} H{\cdot}OH \\ H{\cdot}OH \end{matrix} = \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} + 2HBr.$$

They are also formed by the direct combination of the olefine hydrocarbons with hydrogen peroxide, or by oxidation of the

olefines by potassium permanganate: $C_2H_4 + H_2O + O = C_2H_4(OH)_2$.

The glycols are mostly syrupy, sweet-tasting liquids of relatively high boiling point. They are readily soluble in water and alcohol, insoluble in ether. The double tertiary glycols, known specially as "pinacones," are, however, solid crystalline compounds.

Ethylene Glycol, $CH_2OH.CH_2OH$, is prepared from ethylene bromide, $C_2H_4Br_2$, and water in the presence of potassium carbonate. It is formed also along with trimethylamine on boiling an aqueous solution of cholin, a decomposition product of lecithin and protagon (see p. 850): $C_5H_{15}NO_2 = (CH_3)_3N + C_2H_4(OH)_2$. It is a sweetish, syrupy liquid, boiling at 197°.

Propylene Glycols, $C_3H_6(OH)_2$. —Two isomeric forms are known, *α*-propylene glycol, $CH_3.CH(OH).CH_2OH$, and *β*-propylene glycol, $CH_2OH.CH_2.CH_2OH$. The former of these can be prepared from propylene bromide, but is most easily obtained by distilling glycerin with caustic soda. It boils at 188°, and is converted by fissure ferments into a dextro- and a lævo-rotatory modification; the *β*-propylene glycol is also known as trimethylene glycol, and may be prepared from trimethylene bromide, or produced in the fissure fermentation of glycerin. It boils at 216°.

Hexylene Glycols, $C_6H_{12}(OH)_2$.—The most interesting compound of this formula is the so-called "pinacone," or tetramethyl-ethylene glycol, $\begin{matrix} C(OH)=(CH_3)_2 \\ | \\ C(OH)=(CH_3)_2 \end{matrix}$. It is most readily formed when acetone is reduced by metallic sodium in the presence of potassium carbonate. It forms a white, crystalline mass, with camphor-like odor, melting at 42° and boiling at 171°–172°. By oxidation it is reconverted into acetone.

Other glycols of high molecular weight are found in the natural waxes. Thus, from carnauba wax has been obtained a glycol of the formula $C_{25}H_{50}(OH)_2$, melting at 103.5°, and the white wax obtained from the cochineal insect under the name of *coccerin* on saponification yields *cocceryl alcohol*, $C_{30}H_{60}(OH)_2$.

5. Triatomic Alcohols, or Glycerins. General formula, $C_nH_{2n-1}(OH)_3$.—When three atoms of hydrogen in a hydrocarbon of the paraffin series are replaced by OH groups, we have a triatomic alcohol, or *glycerin*. Such alcohols act like triacid bases, and can combine with one, two, or three molecules of a monobasic acid.

The glycerins are colorless, syrupy liquids, readily soluble in water, and of high boiling point.

The first of the series, that derivable from methane, is unknown. Its formula, $CH(OH)_3$, would be too unstable to allow of its isolation, as a molecule of water would undoubtedly split off from the three OH groups here indicated as attached to the same carbon atom. Its ethyl ester, $CH(OC_2H_5)_3$, is, however, known under the name of orthoformic ether (see p. 639).

The second glycerin of the series corresponding to ethane is also unknown. Its formula, $C_2H_3(OH)_3$, also indicates that to one of the carbon atoms two OH groups would be attached, which gives us an unstable molecule. Its ethyl ester, $C_2H_3(OC_2H_5)_3$, is also known under the name of otho-acetic ether.

Propenyl Glycerin, $C_3H_5(OH)_3$ (**Glycerinum**, U. S. P.), is the triatomic alcohol corresponding to propane, and has the structural formula, $CH_2OH—CHOH—CH_2OH$. It occurs abundantly in nature in combination with the so-called fatty acids as esters of these latter, making up the bulk of the vegetable and animal fats and oils (see p. 674).

It is also produced in the alcoholic fermentation of sugar, and hence is found in most alcoholic beverages. It is also present in the urine as glycerin-phosphoric acid, a decomposition product of lecithin and protagon. It may be formed artificially by the action of water at 170° upon trichlorhydrin (trichlorpropane), $C_3H_5Cl_3$.

Practically, it is always obtained by the decomposition of the fats in connection with the manufacture of soaps and stearic acid. This decomposition may be effected by the aid of water in the form of superheated steam, by alkalies and metallic oxides, or by heating with sulphuric acid. For a fuller account of these methods, see section on Fat Industries.

The pure glycerin is a thick, colorless liquid, of specific gravity 1.27. It solidifies at low temperatures to monoclinic crystals, which fuse at 20° C. It boils at 290°, but in its ordinary impure state cannot be distilled at ordinary pressures without decomposition. It is very hygroscopic, and mixes with water and alcohol in all proportions. It is insoluble in ether, chloroform, carbon disulphide, benzine, benzene, and fixed or volatile oils. It is an excellent solvent for a great range of substances, such as bromine and iodine, alkaline chlorides, fixed alkalies, some of the alkaline earths, as lime, and a number of neutral salts. It also is said to have antiseptic properties.

Both glycerin and its naturally occurring compounds, the fats, decompose when heated, with the production of acrid penetrating vapors of acrolein and similar products.

The present annual production of raw glycerin throughout the world amounts to 40,000 tons, of which 26,000 tons are obtained from the stearic acid manufacture and 14,000 tons from soap manufacture.

Butenyl Glycerins, $C_4H_7(OH)_3$.—Two isomeric compounds of this class have been obtained. The normal compound, $CH_3.CHOH.CHOH.CH_2OH$, is a sweet, syrupy liquid, boiling at 172°–175° under a pressure of 27 millimeters.

Amyl Glycerin, $C_5H_9(OH)_3$, has also been obtained as a thick, syrupy liquid, of a sweet and aromatic taste.

Hexyl Glycerins, $C_6H_{11}(OH)_3$.—Three isomeric compounds of this formula have been obtained, all of which are thick liquids, which can only be distilled under reduced pressure.

6. Tetratomic Alcohols. General formula, $C_nH_{2n-2}(OH)_4$.—If four hydrogen atoms of a saturated hydrocarbon be replaced by four OH groups, we obtain a tetratomic alcohol, which corresponds to a tetracid base. While the four OH groups characteristic of these alcohols seem to require at least four carbon atoms in the molecule, and hence no stable tetratomic alcohols can be expected from methane, ethane, or propane, yet ethers from these lower hypothetical alcohols have been obtained. Thus, ortho-carbonic ether, $C(OC_2H_5)_4$, a liquid of ethereal odor, boiling at 159°, corresponds to an alcohol, $C(OH)_4$.

Erythrite (or Phycite), $C_4H_6(OH)_4$, occurs free in *Protococcus vulgaris*, and combined with orsellic acid as an ester (erythrin) in many lichens and algæ. It forms large quadratic crystals, easily soluble in water, difficultly soluble in alcohol, and insoluble in ether. They fuse at 112° and boil at 330°.

Pentaerythrite, $C_5H_8(OH)_4$, has been made artificially by the action of lime upon a mixture of formic and acetic aldehydes in aqueous solution:

$$3CH_2O + C_2H_4O + H_2 = C_5H_{12}O_4.$$

It crystallizes in large prisms, melting at 250°–255°, and is only moderately soluble in water.

7. Pentatomic Alcohols. General formula, $C_nH_{2n-3}(OH)_5$.—Pentatomic alcohols have not been found in nature, and until very recently had not been obtained artificially. They have been

obtained, however, in several cases by the reduction of certain *pentoses* (see Carbohydrates).

Arabite, $CH_2OH—(CH.OH)_3—CH_2OH$, has been prepared by the reduction of arabinose, $C_5H_{10}O_5$, with the aid of sodium amalgam. It fuses at 102°, and has a lævo-rotatory power in aqueous solution on the addition of borax.

Xylite, $C_5H_{12}O_5$, has been prepared by a similar method from xylose, $C_5H_{10}O_5$. It has not as yet been obtained crystalline, and is optically inactive.

Rhamnite, $C_6H_{14}O_5$, prepared from rhamnose, $C_6H_{12}O_5$, is a homologue of the foregoing. It fuses at 121°, and is right-rotatory in aqueous solution even without the addition of borax.

8. Hexatomic Alcohols. General formula, $C_nH_{2n-4}(OH)_6$. —Several alcohols of the formula $C_6H_{12}O_6$ have been found in nature, and have excited interest because of their close relation to one of the groups of carbohydrates or sugars. The nature of their relation and a method for the synthetic formation of them from these sugars have both been indicated in connection with the classic work of Emil Fischer on the Carbohydrates (see next page).

Mannite, $CH_2OH—(CHOH)_4—CH_2OH$, is found in many plants, as in the larch, in celery, in the leaves of *Syringa vulgaris*, in sugar-cane, in *Agaricus integer* (of the dry substance of which it forms 20 per cent.), in rye bread, and notably in the manna ash (*Fraxinus ornus*), the dried juice of which constitutes **Manna, U. S. P.**

Mannite crystallizes from water in thick rhombic prisms, or from alcohol in silky needles, melts at 165°–166°, is only moderately soluble in water, scarcely soluble in cold alcohol, and insoluble in ether. Its aqueous solution turns the plane of polarization very slightly to the left, but in the presence of borax and other salts it is strongly dextro-rotatory.

It has been obtained artificially by Fischer from both mannose and fructose (lævulose) by reduction with sodium amalgam in neutral or weakly acid solution; when produced from fructose, sorbite, an isomeric alcohol, always accompanies it. Mannite is also formed from some of the sugars in the processes of fermentation, as in the lactic acid fermentation, and in especially large amount in the mucous fermentation of cane sugar.

Fischer has shown that there are three mannites obtainable: the ordinary mannite is the dextro-rotatory variety, and is always obtained in the reduction of *a*-mannose; a lævo-rotatory mannite

is obtained by the reduction of *l*-mannose ; and an inactive mannite is obtained from the inactive mannose. The three varieties, besides differing in their optical characters, differ slightly in their fusing points and in their crystalline forms.

Sorbite, $C_6H_8(OH)_6$, is found in the berries of the mountain ash and in the fruit of the plum, cherry, apple, pear, etc. It crystallizes out of water in small, colorless needles, which contain water of crystallization. The anhydrous substance fuses at 110°–111°. It is slightly lævo-rotatory in simple aqueous solution, but in the presence of borax is dextro-rotatory. It has been prepared synthetically from dextrose, and represents the dextro variety of sorbite only, the lævo-sorbite having been also.

Dulcite (Melampyrite), $C_6H_8(OH)_6$, is found in certain plants like the *Melampyrum nemorosum*, but more particularly in the manna from Madagascar. It crystallizes in monoclinic prisms, fuses at 188.5°, and is still more difficultly soluble in water than mannite. Dulcite is optically inactive and not capable of being resolved into active modifications.

Rhamno-hexite, $C_7H_{10}(OH)_6$, a homologue of the preceding, has been prepared from rhamno-hexose, $C_7H_{14}O_6$. It crystallizes from hot alcohol in small, colorless prisms, melting at 173°, and is dextro-rotatory.

9. Heptatomic to Nonatomic Alcohols.—Starting with the group of sugars (hexoses) corresponding to the hexatomic alcohols, Emil Fischer has built up synthetically several alcohols of higher classes. Thus, the addition of hydrogen cyanide to a hexose will give what is termed a nitrile ; this when saponified yields an acid with seven carbon atoms, which can be reduced by sodium amalgam in successive steps to a sugar and a heptatomic alcohol. We may illustrate this in the case of mannose :

(1)	(2)	(3)	(4)	(5)
CHO	CN	COOH	CHO	CH_2OH
$(CH.OH)_4$	CH.OH	$(CH.OH)_5$	$(CHOH)_5$	$(CHOH)_5$
CH_2OH.	$(CH.OH)_4$	CH_2OH.	CH_2OH.	CH_2OH.
	CH_2OH.			
Mannose.	Mannose-cyanhydrin.	Mannosecarboxylic Acid.	Manno-heptose.	Manno-heptite.

In this way an artificial alcohol, *δ-mannoheptite*, $C_7H_{16}O_7$, was prepared by Fischer, and later its identity with the naturally occurring *Perseite* was established.

Perseite is found abundantly in the fruits and leaves of *Laurus persea*. It crystallizes from water in microscopical needles, melt-

ing at 188°. Its aqueous solution alone is inactive, but on the addition of borax becomes strongly dextro-rotatory.

By analogous synthetical reactions to those given above, there has been obtained from mannoheptose an octatomic alcohol, *δ-mannoctite*, $C_8H_{10}(OH)_8$. By the same method, starting from δ-glucose, there have been obtained the following synthetic alcohols: *α-glucoheptite*, $C_7H_{16}O_7$, fusing at 127°–128°; *α-glucooctite*, $C_8H_{18}O_8$, fusing at 141°; and *α-gluconononite*, $C_9H_{20}O_9$, fusing at 194°.

III. Ethers, or Oxides of the Hydrocarbon Radicals.

The ethers may also be considered as the anhydrides of the alcohols. Thus, $2C_2H_5.OH = (C_2H_5)_2O + H_2O$. It may be, however, that two different alcohols can thus be united by the loss of one molecule of water. The resulting ether will then contain two different hydrocarbon radicals united by oxygen. Such a compound would be a mixed oxide. We distinguish, therefore, between the two classes, and have *simple ethers* or oxides of a single radical, and *mixed ethers* or oxides of mixed radicals. In both these cases, however, the radicals are obtained directly from the hydrocarbons by the loss of one or more hydrogen atoms, and are the same as unite with hydroxyl to form the alcohols. These alcohols, it will be remembered, were spoken of as basic hydrates, so the oxides will be basic oxides. Compounds where a basic or alcohol radical is united by oxygen to an acid radical used to be known as *compound ethers*, but, as they are really ethereal salts, they have been given the name of *esters*, to mark the distinction and to separate them clearly from the basic oxides or ethers.

We may distinguish between the ethers of the monatomic alcohols and those of higher alcohols.

1. Ethers of the Monatomic Alcohols.—These may be formed in several ways. By heating the alcohols with sulphuric acid the ethers can readily be obtained. The reaction goes on in two stages, however, as illustrated in the case of ethyl ether:

(*a*) $C_2H_5.OH + SO_2(OH)_2 = SO_2(OH).OC_2H_5 + H_2O.$
(*b*) $SO_2(OH)OC_2H_5 + C_2H_5.OH = C_2H_5.OC_2H_5 + SO_2(OH)_2.$

In the first reaction a compound known as ethyl-sulphuric acid (see p. 669) is formed, which then reacts with a second molecule of alcohol to form ethyl oxide or ether, and sulphuric acid is regenerated. Another general method for ether formation is to treat the halogen derivatives of the hydrocarbons with a sodium

alcoholate or with alcoholic potash: $C_2H_5I + C_2H_5.ONa = C_2H_5.OC_2H_5 + NaI$.

The ethers are very stable. Ammonia, alkalies, dilute acids, and metallic sodium have no action upon them. They can be changed back into the corresponding alcohols by superheating with water in the presence of some acid, such as sulphuric.

Methyl Ether, $(CH_3)_2O$, is prepared from methyl alcohol and sulphuric acid. At ordinary temperatures is a gas, but can be changed by pressure or cold into a mobile liquid. Boils at —21° C., and burns with bluish flame.

Ethyl Ether, $(C_2H_5)_2O$ (**Æther,** U. S. P.), also known popularly as "sulphuric ether," because prepared by the aid of sulphuric acid. It is prepared by the reactions given above. As in these reactions the sulphuric acid is re-formed after serving to convert the alcohol into ether, it would seem as if the process might be kept up continuously. In fact, it is possible with small amounts of sulphuric acid to convert large quantities of alcohol into ether. The method is sometimes called the "continuous etherification process," but a limit is reached in the power of the sulphuric acid because side reactions interfere. Some sulphuric acid is reduced to sulphurous acid, and the slight impurities in the alcohol become carbonized. The temperature of the reaction must be kept as near 140° C. as possible, as at a higher temperature the acid acts dehydrating upon the alcohol, and at a lower temperature alcohol distils over unchanged. The product is washed with milk of lime to remove the sulphurous acid, then rectified, and the water and alcohol removed by chloride of calcium. The official ether is composed of about 96 per cent. by weight of absolute ether and about 4 per cent. of alcohol containing a little water.

To obtain absolute anhydrous ether, it must be treated with metallic sodium and again distilled.

Common ether is a transparent, mobile liquid, having a characteristic ethereal odor, and a burning, sweetish taste. Its specific gravity is 0.725 to 0.728 at 15° C., or 0.714 to 0.717 at 25° C. It boils at about 37° (the absolute ether boils at 34.97°) and melts at —117.4°. It is somewhat soluble in water (1 part in 10 parts water at 15° C.) and miscible in all proportions with alcohol, chloroform, benzine, benzene, fixed and volatile oils. Its vapor is very inflammable and forms an explosive mixture with air. Ether is a solvent for fats, resins, and many alkaloids; for bromine, iodine, phosphorus, and a number of salts. It is used in medicine largely as an anæsthetic.

In the manufacture of ether as carried out on a large scale, two side-products are obtained that may be mentioned. "Light oil of wine" is obtained as a liquid, boiling between 150° and 300°; it is a mixture of ethers, ketones, and hydrocarbons. "Heavy oil of wine," which boils above 300°, is a mixture of esters of sulphuric acid and olefine hydrocarbons.

Hoffmann's Anodyne (**Spiritus Ætheris Compositus**, U. S. P.) is a mixture of ether, alcohol, and ethereal oil.

Methyl-ethyl Ether, $\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\}O$, is an example of the mixed ethers. It is made most conveniently by the action of ethyl iodide upon sodium methylate:

$$C_2H_5I + NaOCH_3 = NaI + \left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\}O.$$

Methyl-ethyl ether is a colorless liquid of peculiar odor, which boils at 11° C. and is very inflammable. Compressed in liquid form in cylinders it comes occasionally into use as an anæsthetic, being recommended by Richardson as a substitute for chloroform.

Allyl Ether, $(C_3H_5)_2O$, is the oxide of the unsaturated radical allyl and corresponds to allyl alcohol, $C_3H_5.OH$. It boils at 82°.

2. Ethers of the Diatomic Alcohols.—We may have several classes of compounds here, either the compounds of the dyad radical and monad radicals like methyl and ethyl linked by oxygen, or the simple oxides of the dyad alcohol radicals. Thus, we have from $C_2H_4(OH)_2$, ethylene glycol, $C_2H_4\left\{\begin{matrix}OH\\OC_2H_5\end{matrix}\right.$ and $C_2H_4(OC_2H_5)_2$, or C_2H_4O, which is simply ethylene oxide.

Ethylene Oxide, $\begin{matrix}CH_2\\CH_2\end{matrix}>O$, may be obtained by decomposing the halogen derivatives of the glycols by aqueous alkalies. It is isomeric with acetaldehyde (see p. 643), but does not reduce ammoniacal silver solution as does aldehyde. It is a strong base, and precipitates the hydrates of magnesium, aluminum, copper, and iron from the salts.

3. Ethers of the Triatomic and Tetratomic Alcohols.—While methenyl glycerin, $CH(OH)_3$, is unknown in the free state, as stated before (see p. 633), its ethyl ether is known. The so-called *orthoformic ether*, $CH(OC_2H_5)_3$, is this compound. Boiling point, 145°–146°. From propenyl glycerin or common glycerin, $C_3H_5(OH)_3$, we have similarly three ethers: $C_3H_5(OH)_2OC_2H_5$, $C_3H_5(OH)(OC_2H_5)_2$, and $C_3H_5(OC_2H_5)_3$. The first of

the tetratomic alcohols, $C(OH)_4$, was also stated to be unknown in the free state, but its ethyl ether is known under the name of *ortho-carbonic ether*, $C(OC_2H_5)_4$. It is an aromatic-smelling compound, boiling at 158°–159°.

IV. Sulpho-Alcohols, Sulpho-Ethers, and Sulphonic Compounds.

The sulpho-alcohols have long been known under the name of *mercaptans* (from *mercurio aptum*, because of the readiness with which they combine with mercuric oxide), and contain the radical SH in combination with the hydrocarbon radical, instead of OH as in alcohols. They are formed by the action of potassium sulphydrate upon the iodides of the paraffin hydrocarbons. Thus, $C_2H_5I + KSH = C_2H_5SH + KI$.

The combinations of the mercaptans with metallic oxides are known as *mercaptides*. They also combine with aldehydes and ketones, producing in the former case *mercaptals*, and in the latter *mercaptols*. The mercaptans when oxidized yield the *sulphonic acids*, compounds containing the group HSO_3 in combination with the hydrocarbon radical. Thus, $C_2H_5SH + O_3 = C_2H_5.HSO_3$. On the other hand, the oxidation of the mercaptols yields the class of *sulphonals*.

The mercaptans are liquids of most unpleasant and piercing odor, resembling that of leeks. They are nearly insoluble in water, and the lower members are very volatile. They are inflammable.

Methyl Mercaptan, CH_3SH, is a liquid of unpleasant odor, boiling at 6° C. It is formed by the action of anaërobic micro-organisms upon albumen, and is, therefore, found among human intestinal gases.

Ethyl Mercaptan, $C_2H_5.SH$, is a liquid which boils at 36.2°, and is of extremely unpleasant odor. It is now made on a large scale as furnishing the starting-point for the manufacture of sulphonal.

The thio-ethers, or sulphur ethers, are made by distillation of the iodides of the hydrocarbon radicals with potassium sulphide: $\begin{matrix}CH_3I\\CH_3I\end{matrix} + K_2S = \begin{matrix}CH_3\\CH_3\end{matrix}>S + 2KI$.

They are colorless liquids, of unpleasant odor, which are soluble in alcohol but not in water. By their oxidation they yield first *sulphoxides* and then *sulphones:* $(CH_3)_2S$; $(CH_3)_2SO$; $(CH_3)_2SO_2$.

The most important of the thio-ethers is :

Allyl Sulphide, $(C_3H_5)_2S$, known as "garlic oil," is obtained from the leaves of the garlic (*Allium sativum*) and the seeds of many of the Cruciferæ. It probably does not exist originally as such, but results as a decomposition product from more complicated materials. It boils at 140°. It can also be formed artificially from allyl iodide and potassium sulphide.

The sulphides of propyl, butyl, and amyl have recently been identified by Mabery as present in the crude petroleum of Lima, Ohio, and in Canadian petroleums.

The sulphonic acids and salts contain the sulphonic group, HSO_3, combining directly, with the valence one, with the hydrocarbon radicals. They may be formed by boiling iodides of the hydrocarbon radicals with alkaline sulphites, $C_2H_5I + K_2SO_3 = C_2H_5KSO_3 + KI$, or by the oxidation of mercaptans, sulphides, and sulphocyanates with nitric acid, as before noted.

Methyl-sulphonic Acid, $CH_3.SO_3H$, has been prepared as a syrupy liquid.

Ethyl-sulphonic Acid, $C_2H_5.SO_3H$, forms a deliquescent crystalline solid. A derivative of this, amido-ethyl-sulphonic acid, is known as *taurin*, and is present in the gall, in combination with cholic acid, as taurocholic acid.

Reference was made, under mercaptans, to the fact of their combining with ketones to form mercaptols. This reaction is a fundamental one in the preparation of the important product known as *sulphonal*.

Sulphonal (Diethyl-sulphone-dimethyl-methane), $CH_3>C<\begin{matrix}SO_2C_2H_5\\SO_2C_2H_5\end{matrix}$. This compound is prepared from ethyl mercaptan in two reactions. First, 2 molecules of the mercaptan unite with 1 molecule of acetone, with the elimination of water, to form the corresponding mercaptol. This is then oxidized by an acidified potassium permanganate solution. The reactions are :

$$CH_3>C<O + H\,SC_2H_5 = CH_3>C<SC_2H_5 + H_2O.$$
$$\qquad\qquad H\,SC_2H_5 \qquad\qquad\quad SC_2H_5$$

$$CH_3>C<SC_2H_5 + O_4 = CH_3>C<SO_2C_2H_5.$$
$$\qquad SC_2H_5 \qquad\quad\; SO_2C_2H_5$$

Sulphonal forms colorless, odorless, and tasteless crystals, melting at 125°–126°, and boiling, with slight decomposition only, at 300°. More soluble in hot than in cold water ; soluble in boiling

alcohol. The solutions have a neutral reaction. If a small quantity of sulphonal be heated in a small test-tube with powdered charcoal, the characteristic odor of mercaptan is obtained. It is used very successfully as an hypnotic and soporific.

Trional (Diethyl-sulphone-methyl-ethyl-methane), $\begin{matrix}CH_3\\C_2H_5\end{matrix}>C<\begin{matrix}SO_2C_2H_5\\SO_2C_2H_5\end{matrix}$. If, instead of acetone (dimethyl-ketone), we take methyl-ethyl-ketone for the reaction with mercaptan, we obtain the product known as trional, which forms colorless, lustrous, and odorless crystals, melting at 76°, soluble in hot water, easily soluble in alcohol and ether. Its therapeutic action is similar to that of sulphonal, but it is said to act more rapidly and in smaller doses.

Tetronal (Diethyl-sulphone-diethyl-methane), $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}>C<\begin{matrix}SO_2C_2H_5\\SO_2C_2H_5\end{matrix}$, is made by using diethyl-ketone (propione) instead of acetone for the reaction with mercaptan. It forms colorless, lustrous scales, which melt at 85°, easily soluble in boiling water and in alcohol, and moderately soluble in ether. It is very similar in its action to trional.

V. Aldehydes and Ketones.

In speaking of these compounds under the head of Classification of Organic Compounds (see p. 605), they were referred to as products of oxidation of the alcohols. They are alike in this common derivation, but differ because of a fundamental difference in the alcohols from which they may be derived. Thus, if a primary alcohol containing the group $-CH_2OH$ is oxidized, it first loses two hydrogen atoms, and we have the group $-CO.H$, characteristic of aldehydes; if, on the other hand, a secondary alcohol containing the group $\begin{matrix}|\\CH.OH\\|\end{matrix}$ is oxidized, it loses two hydrogen atoms, and we have the group $\begin{matrix}|\\CO\\|\end{matrix}$, characteristic of ketones. Conversely, by the action of sodium amalgam upon aldehydes we get primary alcohols, while the action of the same reagent upon ketones gives us secondary alcohols. Another important difference between the two classes is, that aldehydes readily and in some cases spontaneously pass to a fuller stage of oxidation, viz., acids, in which the $-CO.H$ group is changed to a $-CO.OH$ group, while the ketones represent the final products of oxidation of the secondary alcohols.

They have some reactions in common and some which are distinctive of each class. Both aldehydes and ketones combine with alkaline bisulphites to form crystalline compounds, which, therefore, serve for their extraction and purification when admixed with other organic compounds. Both combine with hydrocyanic acid to form addition compounds known as *nitriles*, which, when saponified, yield acids by the change of the CN group to COOH. Both react with mercaptans (see p. 640). Both unite with hydroxylamine, $NH_2.OH$, to form *oximes*, known respectively as *aldoximes* and *ketoximes;* and both unite with hydrazines (see Phenylhydrazine, p. 755) to form a class of compounds called *hydrazones*.

The most important of the reactions which are characteristic of aldehydes alone are the reducing action upon ammoniacal silver solutions, whereby a silver mirror is obtained, and the formation of crystalline addition compounds with ammonia.

1. **Aldehydes of Saturated Alcohols.** General formula, $C_nH_{2n}O$.

Formaldehyde, HCO.H.—A mixture of gaseous methyl alcohol and air is led over gently-heated copper oxide, and the liquid obtained is carefully fractioned. It is a gas of pungent odor, condensible to a liquid boiling at —21°, which reduces ammoniacal silver solution in the cold. It polymerizes very readily to form paraformaldehyde, $C_3H_6O_3$, a white crystalline mass, or under other conditions to produce a substance known as "formose," from which Emil Fischer has isolated *α-acrose*, a sugar of the formula $C_6H_{12}O_6$.

Under the name of "Formalin" a 40-per-cent. aqueous solution of formaldehyde has been introduced into medicine. It is claimed for it that it is a non-poisonous antiseptic of great power, and as such has been used in surgical practice as well as for the preservation of foods and drinks.

Acetaldehyde, $CH_3.COH$. — This compound, obtained from common, or ethyl, alcohol, was first called aldehyde from *alcohol dehydrogenatum*, to indicate that its formula differed from that of alcohol in having lost two hydrogen atoms. It is found in both crude wood-spirit and grain-spirit, from the latter of which it can be obtained in the first running of the rectifying stills. It is most generally obtained, however, by the oxidation of ethyl alcohol with the aid of sulphuric acid and potassium dichromate or manganese dioxide. Ammonia gas is passed into an ethereal solution of this crude distillate, and the crystalline aldehyde-ammonia

separated out. This compound is distilled with dilute sulphuric acid, when pure aldehyde can be collected. It is a colorless, mobile liquid, boiling at 21°, of a sharp and suffocating odor. In contact with a little hydrochloric or sulphuric acid or zinc chloride it quickly polymerizes and yields

Paraldehyde, $(C_2H_4O)_3$ (**Paraldehydum**, U. S. P.).—This is a colorless, transparent liquid, with a strong, characteristic, but not unpleasant odor, and a burning and cooling taste. It melts at 10° C., and boils at 123°–125°. It is soluble in 8.5 parts of water, and miscible in all proportions with alcohol, ether, and fixed or volatile oils.

Another polymeric form of aldehyde is *Metaldehyde*, $(C_2H_4O)_x$, which is produced from aldehyde at low temperatures, and is crystalline, subliming at 112°–115°. When heated to 120° under pressure it changes back to aldehyde.

By the action of chlorine upon alcohol chlorine substitution derivatives of aldehyde are formed, one, two, or three hydrogen atoms being replaced by chlorine. The most important of these derivatives is *Trichloraldehyde* (or Chloral), $CCl_3.COH$. This is an oily liquid, boiling at 98° C., of sharp, characteristic odor, which combines with sodium bisulphite, ammonia, and hydrogen cyanide like aldehyde, and like it reduces an ammoniacal silver solution. It crystallizes with one molecule of water to form

Chloral Hydrate (**Chloral**, U.S.P.), $CCl_3.COH + H_2O$.—The facts that chloral and water combine with development of heat, and that certain reactions given with chloral are not obtained with chloral hydrate, make it possible that this solid is not a mere hydrate, but a true chemical compound. It forms monoclinic crystals, fusing at 57° and boiling at 97°. It is freely soluble in water, alcohol, or ether; also in chloroform, benzine, benzene, carbon disulphide, and fixed and volatile oils.

Chloral is manufactured on a large scale by saturating ethyl alcohol with chlorine, first in the cold and afterwards with the aid of heat. After cooling there separates out a crystalline mass known as *chloral-alcoholate*, $CCl_3.CH<\begin{matrix}OH\\OC_2H_5\end{matrix}$. This is then heated with strong sulphuric acid, and when hydrochloric acid gas no longer escapes the chloral is distilled off. It is again rectified and mixed with the water necessary for the formation of the chloral hydrate. The action of chlorine upon alcohol is said to be aided by the presence of substances known as "chlorine car-

riers," like iodine. Ferric chloride also has been proposed, in which case it is said that the chloral-alcoholate is not formed as an intermediate product.

One of the most important reactions of chloral is its decomposition by alkalies and the resulting production of chloroform, according to the reaction: $CCl_3.COH + NaOH = CHCl_3 + HCOONa$, whereby chloroform and sodium formate result. The purest chloroform is now made by this method from crystallized chloral hydrate. Chloral hydrate is an important hypnotic and sedative.

Among the compounds of chloral that deserve mention because of their proposed use in medicine are:

Chloral Cyanhydrate, $CCl_3.COH.HCN$, which forms white, crystalline masses, smelling like chloral hydrate, and melting at 61°. This compound has been recommended for use instead of bitter-almond water, as 6.46 grammes of it will contain uniformly 1 gramme of anhydrous prussic acid.

Chloral Ammonium, $CCl_3.CH(OH)NH_2$, forms fine, white needles, fusing at 82°–84°; nearly insoluble in cold water, decomposed by hot water, easily soluble in alcohol and ether. Said to be a good hypnotic and analgesic.

Chloralimide, $CCl_3.CH{=}NH$, differs from the preceding by the loss of the elements of water. Crystalline compound slightly soluble in water, soluble in alcohol and ether. Used as an hypnotic.

Chloralformamide (*Chloralamide*), $CCl_3.CHO.HCONH_2$, is a compound of chloral and formamide (see p. 684). It forms white, lustrous crystals, melting at 114°–115°; slowly soluble in cold water, decomposed by hot water, readily soluble in alcohol. Used as a soporific, being decomposed in the blood into chloral and ammonium formate.

Chloralose, $C_8H_{11}Cl_3O_6$, is the name given to a compound obtained by heating chloral and glucose, according to the reaction:

$$CCl_3.CO.H + C_6H_{12}O_6 = C_8H_{11}Cl_3O_6 + H_2O.$$

It forms fine, colorless needles, melting at 184°–185°; difficultly soluble in cold water, more easily in warm water, easily soluble in alcohol. It is recommended as an hypnotic.

Chloral also combines with antipyrin in two proportions, the monochloral-antipyrine (or *hypnal*) and the bichloral-antipyrine.

Neither bromal, $CBr_3.COH$, nor iodal, $CI_3.COH$, has found any use in medicine.

Butyraldehyde, $CH_3.CH_2.CH_2.COH$, results from the oxidation of butyl alcohol. It is also obtained by the oxidation of albuminoids by chromic acid. Its chlorine derivative :

Butyl Chloral, $C_4H_5Cl_3O$, also forms a hydrate which has been used in medicine as a substitute for chloral hydrate.

Œnanthaldehyde (Œnanthol), $C_7H_{14}O$, is an aldehyde obtained in quantity by the distillation of castor oil under reduced pressure, as the ricinoleic acid of the oil splits up, according to the reaction :

$$C_{18}H_{34}O_3 = C_7H_{14}O + C_{11}H_{20}O_2.$$

Œnanthol is a strongly refracting liquid of penetrating aromatic odor. Used in the manufacture of higher fruit ethers (see p. 670).

2. Aldehydes of Unsaturated Alcohols, $C_nH_{2n-2}O$.—These correspond to the unsaturated alcohols derived from the olefine hydrocarbons. They are, of course, unsaturated bodies also.

Acrolein, $CH_2{=}CH.COH$, is the aldehyde corresponding to allyl alcohol, $C_3H_5.OH$. It is produced whenever glycerin is decomposed with loss of water ; hence, in the superheating or distillation of the fats, as shown in the reaction $C_3H_5(OH)_3 - 2H_2O = C_3H_4O$. Liquid of sharp, irritating odor, causing tears, boiling at 52.4°.

Croton Aldehyde, C_4H_6O.—The next aldehyde in this series is found in the first runnings of raw spirits. Sharp-smelling liquid, boiling at 104°–105°. Reduces silver oxide, and is thereby oxidized to crotonic acid.

3. Acetals.—The acetals result from the union of alcohol with aldehydes with the elimination of water, or from the oxidation of the alcohols when they are produced along with the aldehydes.

Methylal, $HCH{<}\begin{matrix}OCH_3\\OCH_3\end{matrix}$, is obtained by oxidizing methyl alcohol with sulphuric acid and manganese dioxide, fractioning the product, and collecting the fraction boiling between 40° and 50°. Mobile, colorless liquid, of penetrating, aromatic odor, boiling at 42°. It is soluble in water, alcohol, ether, and fixed and ethereal oils. Used in medicine as an hypnotic.

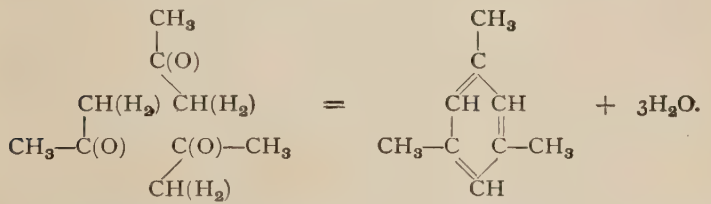
Acetal, $CH_3.CH{<}\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}$, is formed by the reaction :

$$CH_3.CHO + \begin{matrix}H.OC_2H_5\\H.OC_2H_5\end{matrix} = CH_3.CH{<}\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix} + H_2O.$$

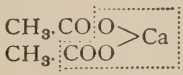
Is found also in the raw grain spirit when filtered through charcoal. Colorless liquid of agreeable taste, boiling at 104°, slightly soluble in water, very soluble in alcohol and ether.

4. Ketones.—The ketones are most readily distinguished from the aldehydes by their behavior to oxidizing agents. They are not affected by weak oxidizing agents; hence ammoniacal silver solution is not reduced by them as it is by aldehydes. Chromic acid and energetic oxidizing agents act upon them, but the ketone molecule is broken up thereby, and they yield acids with a smaller number of carbon atoms. Thus, acetone, $CH_3—CO—CH_3$, when oxidized yields acetic acid, CH_3COOH, CO_2, and H_2O.

The ketones show, like the aldehydes, a tendency to condense or polymerize. With acetone this condensation (by heating in the presence of concentrated sulphuric acid) gives rise to mesitylene, an aromatic hydrocarbon:



7 *Dimethyl-ketone* (Acetone), $CH_3—CO—CH_3$, is found in small amount in normal human urine, in the blood, and in secretions; the amount is notably increased in cases of disease like diabetes mellitus. It is contained in crude wood-spirit, and is a product of the distillation of sugar, gums, cellulose, etc. Technically it is obtained by the dry distillation of calcium acetate, according to the reaction:



Is a liquid of ethereal, refreshing odor, boiling at 56° C. Soluble in water, alcohol, and ether. Sodium amalgam reduces it to isopropyl alcohol. A trace of acetone may be detected by the addition of a solution of iodine in potassium iodide along with an alkali, when iodoform is obtained, the odor and color of which are distinctive. Acetone is used largely as a solvent for resins, and in recent years in the manufacture of chloroform (see p. 622).

Methyl-ethyl Ketone, $CH_3.CO.C_2H_5$, is also contained in crude wood-spirit.

Methyl-nonyl Ketone, $CH_3.CO.C_9H_{19}$ is the chief constituent of oil of rue, from *Ruta graveolens*. Oil of pleasant odor, boiling at 224°. Yields on oxidation acetic and nonylic (pelargonic) acids, the latter of which is used in the manufacture of fruit ethers.

VI. Acids and Derivatives of Acids.

In speaking of the distinction between aldehydes and ketones (see p. 642), mention was made of the fact that aldehydes as the product of the oxidation of primary alcohols did not represent the final result of oxidation, but that the COH group of the aldehyde readily changed to a COOH group by a more complete oxidation. We may illustrate this by the example of ethyl alcohol: $CH_3.CH_2OH$, ethyl alcohol; $CH_3.COH$, acetaldehyde; CH_3COOH, acetic acid.

The group which is taken as characteristic of the acid is —CO.OH, known as "carboxyl," and the presence of one such group gives us a monobasic organic acid. If the alcohol contain two groups $—CH_2OH$, as in diatomic alcohols, the complete product of oxidation will contain two groups —COOH, and we shall have a dibasic acid.

The organic acids, like the alcohols, are hydrates,—that is, contain the OH group combined with a radical,—but they are acid hydrates instead of basic hydrates. Therefore the radical which is present combined with the —OH is spoken of as an acid radical, while the alcohol radical was a basic radical. We shall see that the acid radical always bears a very simple relation to the alcohol or basic radical from which it has been derived. What the difference is may be seen by comparing the formulas given above. Ethyl alcohol, CH_3CH_2OH, contains the radical *ethyl*, C_2H_5, combined with OH, while acetic acid, $CH_3.CO.OH$, contains the radical *acetyl*, CH_3CO, combined with OH. The acid radical we find to be formed from the alcohol radical by the exchange of two H atoms for an O atom.

1. Saturated Monobasic Acids (*Fatty Acid Series*), $C_nH_{2n}O_2$.—These are formed from the primary monatomic alcohols of the paraffin series by oxidation. They may also be formed from the cyanides of the hydrocarbon radicals next lower in the series by saponification, as in the reaction:

$$CH_3.CN + 2H_2O = CH_3.COOH + NH_3;$$

that is, methyl cyanide will yield acetic acid and ammonia. By this means we may pass up the series from one hydrocarbon or

alcohol radical to the acid corresponding to the next higher hydrocarbon.

The higher members of this series of acids occur abundantly in nature, in the natural fats and oils combined with glycerin, and in the waxes with monatomic alcohols as base, to form esters or salts.

TABLE OF THE SATURATED MONOBASIC ACIDS (FATTY ACIDS).

Name.	Formula.	Melting Point.	Boiling Point.
Formic	$H.COOH$	9° C.	99°
Acetic	$CH_3.COOH$	17°	118°
Propionic	$CH_3.CH_2.COOH$	—36°	141°
Butyric, Normal	$CH_3.(CH_2)_2.COOH$	0°	163°
Butyric, Iso	$(CH_3)_2{=}CH.COOH$	—79°	154°
Valeric, Normal	$CH_3.(CH_2)_3.COOH$	—58°	186°
Valeric, Iso	$(CH_3)_2{=}CH.CH_2.COOH$	—51°	175°
Methyl-ethyl-acetic	$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>\!CH.COOH$	Liquid.	177°
Trimethyl-acetic	$(CH_3)_3{=}C{-}COOH$	35°	164°
Caproic	$C_6H_{12}O_2$	—2°	205°
Œnanthic	$C_7H_{14}O_2$	—10°	224°
Caprylic	$C_8H_{16}O_2$	16°	236°
Pelargonic	$C_9H_{18}O_2$	12°	254°
Capric	$C_{10}H_{20}O_2$	31°	269°
Undecylic	$C_{11}H_{22}O_2$	28°	*213°
Lauric	$C_{12}H_{24}O_2$	44°	*226°
Tridecylic	$C_{13}H_{26}O_2$	40°	*236°
Myristic	$C_{14}H_{28}O_2$	54°	*248°
Pentadecylic	$C_{15}H_{30}O_2$	51°	*257°
Palmitic	$C_{16}H_{32}O_2$	62°	*269°
Margaric	$C_{17}H_{34}O_2$	60°	*277°
Stearic	$C_{18}H_{36}O_2$	69°	*287°
Nondecylic	$C_{19}H_{38}O_2$	66°	*298°
Arachidic	$C_{20}H_{40}O_2$	77°	. .
Behenic	$C_{22}H_{44}O_2$	76°	. .
Lignoceric	$C_{24}H_{48}O_2$	80°	. .
Cerotic	$C_{27}H_{54}O_2$	78°	. .
Melissic	$C_{30}H_{60}O_2$	90°	. .

* Boiling points under a pressure of 100 mm.

Formic Acid, HCO.OH, was first obtained from the bodies of ants (*Formica rufa*), whence the name. It also occurs in the bristles of the stinging nettle, the fruit of the soap-tree, and in tamarinds and fir-cones ; also in perspiration, urine, and the juice of flesh. It is made artificially by a variety of reactions, some of which are direct syntheses from inorganic materials. Thus, the action of moist carbon monoxide upon dry sodium hydrate (or, better, granular soda-lime) at temperatures of 160°–200°, will

give us a rapid and abundant production of sodium formate: $CO + NaOH = HCO.ONa$.

It may also be obtained by the oxidation of methyl alcohol; by the reaction of water upon hydrogen cyanide in the presence of acids or alkalies, according to the reaction $HCN + 2H_2O = HCOOH + NH_3$; by the decomposition of chloroform and chloral by alkalies; or, finally, by the heating of oxalic acid in the presence of glycerin. This method is the one usually employed, as the glycerin is regenerated and so can convert large quantities of oxalic acid into formic acid. The reactions are:

$$C_3H_5(OH)_3 + \begin{matrix}COOH\\|\\COOH\end{matrix} = C_3H_5(OH)_2OCHO + CO_2 + H_2O.$$

$$C_3H_5(OH)_2OCHO + H_2O = HCOOH + C_3H_5(OH)_3.$$

Formic acid is a colorless liquid with penetrating odor. The liquid produces a painful inflammation if dropped upon the skin, but acts as a powerful antiseptic in dilute solution. Formic acid in solution may be recognized by the reducing power it exerts upon silver and mercury salt solutions. Thus, metallic silver is separated out on heating formic acid with silver nitrate solution, while white calomel is separated out on adding formic acid to corrosive sublimate solution. Formic acid unites with inorganic bases to form salts called *formates*, all of which are easily soluble except the lead and mercurous salts. The formates containing organic bases will be spoken of under "Esters."

Acetic Acid, $CH_3.COOH$, was known to the ancients in the form of wine vinegar, and in a purer and more concentrated form to the alchemists. It is found partly free and partly combined with potassium and calcium in various plant juices, and in the perspiration, milk, urine, muscles, and excrementa of animals. It results from the fermentative decomposition of albuminoids and glue, and the dry distillation of wood, starch, and sugar. A complete synthesis of it has been accomplished by the oxidation of acetylene, which (see p. 618) can be built up from carbon and hydrogen. Thus, $CH{\equiv}CH + H_2O + O = CH_3COOH$.

The two great sources of acetic acid, however, are the acetic fermentation of alcoholic liquids (see Fermentation), and the dry distillation of wood. As made from this latter source it is known as "pyroligneous" acid, and is quite impure from the presence of creosote and other empyreumatic products found in wood-tar. It is purified by neutralizing with milk of lime, whereby the

"brown acetate of lime" is obtained. This is purified by roasting off the tarry impurities, decomposed with hydrochloric acid, and the acetic acid distilled off. It may be further purified by the recrystallization of the sodium salt.

Acetic acid when pure is a strongly acid liquid of pungent odor, burning the skin, and solidifying in the cold to crystalline plates, melting at 17°, and boiling at 118°, sp. gr. at 15° 1.055. This is known as glacial acetic acid (**Acidum Aceticum Glaciale,** U. S. P.). Two other strengths of acid are also official, one containing about 36 per cent. by weight of absolute acetic acid (**Acidum Aceticum,** U. S. P.), and a still more dilute acid containing 6 per cent. by weight of absolute acetic acid (**Acidum Aceticum Dilutum,** U. S. P.).

The glacial acetic acid has a strong solvent power for many organic substances, and hence is frequently used as a solvent from which to crystallize out organic preparations. Acetic acid may be detected by first neutralizing with ammonia and then adding ferric chloride, when a blood-red color of ferric acetate is obtained, which color is destroyed by heating with hydrochloric or sulphuric acids, or by heating with alcohol and sulphuric acid, when the characteristic odor of acetic ether is obtained.

The salts of acetic acid are known as *acetates*. All the neutral salts are soluble in water, but insoluble basic acetates of several of the heavy metals are obtained. The official metallic acetates are :

Potassii Acetas, U. S. P., $KC_2H_3O_2$.—A white, deliquescent salt, odorless, and of a saline taste, readily soluble in water and alcohol.

Sodii Acetas, U. S. P., $NaC_2H_3O_2+3H_2O$. — Colorless, monoclinic prisms, odorless, and of saline taste, efflorescing in dry air. Soluble in water, less readily soluble in alcohol.

Plumbi Acetas, U. S. P., $Pb(C_2H_3O_2)_2 + 3H_2O$.—Forms colorless, shining, transparent, monoclinic prisms, with faintly acetous odor, and a sweetish, astringent, and metallic taste. Efflorescent, and absorbing carbon dioxide in air, easily soluble in water, and moderately soluble in alcohol.

Zinci Acetas, U. S. P., $Zn(C_2H_3O_2)_2+2H_2O$.—Soft, white, monoclinic plates, of pearly lustre, faintly acetous odor, and astringent, metallic taste. Gradually effloresces in the air. Easily soluble in water, moderately soluble in alcohol.

Besides these crystalline salts, we have several acetates official in solution, as **Liquor Ammonii Acetatis,** U. S. P. :

Liquor Ferri Acetatis, U. S. P.; **Liquor Ferri et Ammonii Acetatis**, U. S. P., and **Liquor Plumbi Subacetatis**, U. S. P.

The most important acetates, in addition to those just mentioned, are ferrous acetate, $Fe_2(C_2H_3O_2)_4$, largely used, under the name of "iron liquor," as a mordant in dyeing; aluminum acetate, $Al_2(C_2H_3O_2)_6$, used for the same purpose, under the name of "red liquor;" neutral and basic acetates of copper, $Cu(C_2H_3O_2)_2$ and $Cu(C_2H_3O_2)_2 + CuO$, used, under the name of "verdigris," in paint colors; and a double acetate and arsenite of copper, known as "Paris green."

Propionic Acid, $C_3H_5O.OH$, is so named because it is the first of this series which can be separated from its aqueous solution in an oily layer by the addition of calcium chloride and similar salts, hence πρῶτος, the first, πιων, fat. It is contained in human urine and in perspiration, in the fruit of *Gingko biloba* and other plants, and in crude wood vinegar. It can be formed by the oxidation of propyl alcohol, by the saponification of ethyl cyanide, and by the action of ferments upon glycerin and upon malate and lactate of calcium.

It is a liquid of peculiar odor, boiling at 141° C.

Butyric Acids, $C_4H_7O.OH$.—The two butyl alcohols (see page 562), both being primary alcohols, may yield on oxidation corresponding acids. The normal butyric acid, $CH_3.CH_2.CH_2.COOH$, is found, combined with glycerin, in freshly-made butter, and in the free state in rancid butter. The free acid is also found in perspiration, in the contents of the intestines, and in the fæces. It is also produced readily by fermentation, either from sugar by the butyric fermentation or from albuminoids, like fibrin and casein, or from glycerin by fissure ferments.

Liquid of sharp, rancid odor, boiling at 163°, soluble in water, but separating on addition of calcium chloride.

The isobutyric acid, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH.COOH$, is found in many plants, as in *Ceratonia siliqua*, in the root of *Arnica montana*, and as ester in Roman chamomile oil and croton oil. Liquid smelling like the normal butyric acid, but more sparingly soluble in water, and boiling at 154°.

Valeric Acids, $C_5H_9O.OH$.—The normal valeric acid is found in crude wood vinegar, and may be obtained by the oxidation of the normal amyl alcohol. Liquid smelling like butyric acid, boiling at 184°–185°, and optically inactive.

Isovaleric acid, $\frac{CH_3}{CH_3}>CH.CH_2COOH$, is found abundantly in dolphin oil and in the root of *Valeriana officinalis*. It is also found in human excrement, and is a product of the decomposition of albuminoids, hence its occurrence in old cheese. It may be obtained most readily by the oxidation of the amyl alcohol of fermentation by the aid of sulphuric acid and potassium bichromate. Liquid of strong, unpleasant odor of valerian, boiling at 175°. Several of the metallic valerianates are of importance in medicine. These are:

Ammonii Valerianas, U. S. P., $NH_4C_5H_9O_2$.—Colorless, crystalline plates, with the odor of valerian, of a sharp, sweetish taste, and deliquescent in moist air. Soluble in water, alcohol, and ether.

Ferri Valerianas, U. S. P.—Forms a dark brick-red, amorphous powder, with the odor of valerian, and a mild, styptic taste; permanent in dry air.

Zinci Valerianas, U. S. P., $Zn(C_5H_9O_2)_2+2H_2O$.—White, pearly scales, having the odor of valerianic acid, and a sweetish, astringent, and metallic taste. Not very soluble in water, more soluble in alcohol.

The other varieties of valeric acid are only of theoretical interest as yet.

Caproic Acid, $C_6H_{11}O.OH$.—The normal caproic acid is found in cocoanut oil and Limburg cheese, and is produced in the butyric fermentation of sugar and the oxidation of albuminoids, and as glycerin ester in butter made from goat's milk. Like valeric acid, it has a very persistent and unpleasant odor of perspiration and rancid butter.

Caprylic Acid, $C_8H_{15}O.OH$, is found, with caproic and capric acids, in the butter from goat's milk (whence the names), and in butter, cheese, and wine fusel oil.

Pelargonic Acid, $C_9H_{17}O.OH$, is found among the volatile constituents of the plant *Pelargonium roseum*.

Lauric Acid, $C_{12}H_{24}O_2$, is contained as glyceride in the oil from *Laurus nobilis*, as well as in cocoanut oil, pichurim beans, dika bread, and in spermaceti.

Myristic Acid, $C_{14}H_{28}O_2$, is contained in nutmeg butter and in oil of iris. Small quantities have also been found in butter and in spermaceti.

Palmitic Acid, $C_{16}H_{31}O.OH$, is found abundantly in combination with glycerin as an ester "palmitin" (see p. 672). The acid

is best extracted from Japan wax or from palm oil. It may also be formed by fusing oleic acid or cetyl alcohol with solid potassium hydrate. White scales, fusing at 60°.

Margaric Acid, $C_{17}H_{33}O.OH$, was formerly supposed to be present in the natural fats, but the supposed acid was found to be a mixture of palmitic and stearic acid. Margaric acid has, however, been made synthetically from cetyl cyanide, $C_{16}H_{33}.CN$.

Stearic Acid, $C_{18}H_{35}O.OH$ (**Acidum Stearicum**, U. S. P.), as commercially obtainable, forms a hard, white, somewhat glossy solid, odorless and tasteless, and permanent in the air. Insoluble in water, moderately soluble in cold alcohol, readily soluble in boiling alcohol and ether. Stearic acid melts at 69.2° C.

Arachidic Acid, $C_{20}H_{39}O.OH$, is present in earth-nut oil (from *Arachis hypogæa*). It is also contained in cacao oil.

Lignoceric Acid, $C_{24}H_{47}O.OH$, is found in the free state in the paraffine of beechwood tar, and as glyceride in earth-nut oil.

Cerotic Acid, $C_{27}H_{53}O.OH$, is found in the free state as the chief constituent of beeswax, also as the ceryl ester in Chinese wax, and in wool suint. It is also obtained by the oxidation of paraffine with chromic acid or dilute nitric acid.

Melissic Acid, $C_{30}H_{59}O.OH$, is obtained from myricyl alcohol by fusion with potassium hydrate or soda-lime. It is also found free in beeswax.

2. Unsaturated Monobasic Acids (*Oleic Acid Series*), $C_nH_{2n-2}O_2$.—These acids are the derivatives of the olefine hydrocarbons and the unsaturated monatomic alcohols of the formula $C_nH_{2n}O$. Being unsaturated, they can combine directly with two atoms of halogen, and in some cases two atoms of hydrogen or one molecule of haloid acid. Upon this reaction is based the method of the quantitative analysis of fatty oils by determining the "iodine figure" or the "bromine figure," showing the percentage of unsaturated acids present. The acids of this series may be formed by the oxidation of the corresponding alcohols or aldehydes, by saponifying the cyanides of the unsaturated alcohols, thus forming the acid next higher in the series, and lastly, by heating the monohalogen substitution products of the saturated fatty acids with alcoholic potash.

The lowest members of the series are only obtained synthetically; the higher ones, on the other hand, are found as glycerides in animal and vegetable fats.

Acrylic Acid, $C_3H_4O_2$.—By the oxidation of either allyl alcohol or acrolein. Generally obtained from β-iodopropionic acid, which

is distilled with oxide of lead. Unpleasant, acrid, and penetrating smelling liquid. Crystallizes when cooled. Boiling point 140°; easily soluble in water.

Crotonic Acid, $C_4H_6O_2$.—Three isomeric varieties are known, of which the first and the second occur in crude pyroligneous acid, while the third is found in Roman chamomile oil.

Angelic Acid and *Tiglic Acid*, $C_5H_8O_2$.—The former of these isomeric acids is found in angelica root as well as in Roman chamomile oil, where it is present as an ester; the latter, also, in the Roman chamomile oil as amyl ester.

Hypogæic Acid and *Physetolic Acid*, $C_{16}H_{30}O_2$.—The former of these isomeric acids is found in the fruit of the earth-nut (*Arachis hypogæa*) as glyceride, and forms crystals, melting at 33°; the latter is found in sperm oil (from the head of *Physeter macrocephalus*), and melts at 30°. The first acid yields, on distillation, sebacic acid, while the second does not yield this product; the first is changed by nitrous acid into an isomeric modification, the second is not affected by nitrous acid.

Oleic Acid, $C_{18}H_{34}O_2$ (**Acidum Oleicum**, U. S. P.), is found abundantly in nature as glyceride in all the fat oils, both vegetable and animal. A colorless oil, forming white needles when chilled. Melting point 14°. The oil has a sp. gr. of about 0.900 at 15° C. It is insoluble in water, soluble in alcohol, chloroform, benzene, benzine, oil of turpentine, and fixed and volatile oils. It cannot be vaporized without decomposition. A small quantity of nitrous acid changes it into the isomeric *Elaidic acid*, which is white and crystalline, fusing at 45°.

Döglinic Acid, $C_{19}H_{36}O_2$, found as glyceride in the oil of *Balæna rostrata* (dögling whale). Oil solidifying at low temperatures.

Erucic Acid, $C_{22}H_{42}O_2$, is found in black and white mustard seed oil. It forms needles melting at 33°–34°. With a small quantity of nitrous acid, is changed into the isomeric *brassidic acid*.

3. **Unsaturated Monatomic Acids** (*Propiolic Acid Series*), $C_nH_{2n-4}O_2$.—The acids of this series correspond to the acetylene hydrocarbons, and are capable of adding on four atoms of halogens like iodine. They may be formed by the direct addition of carbon dioxide to the sodium compounds of the acetylene hydrocarbons, as:

$$\underset{\text{Acetylene-sodium.}}{CH{\equiv}CNa} + CO_2 = \underset{\text{Propiolate of Sodium.}}{CH{\equiv}C.COONa.}$$

Propiolic Acid, $C_3H_2O_2$.—In physical characters very similar to propionic acid. Forms silky needles melting at 6°, and boils at 144°. Easily soluble in water and alcohol.

Tetrolic Acid, $C_4H_4O_2$, and *Sorbic Acid*, $C_6H_8O_2$, follow in this series.

Linoleic Acid, $C_{18}H_{32}O_2$, is found as glyceride in linseed oil (from the seeds of *Linum usitatissimum*). A yellow oil, rapidly resinifying in the air. This acid is important as the basis of "drying oils."

Supplement to the Unsaturated Acids:

Ricinoleic Acid, $C_{18}H_{34}O_3$, the characteristic acid of castor oil, is very similar to oleic acid, but contains one alcoholic OH group. It is oily and solidifies at —6° to —10°. It does not absorb oxygen from the air, and hence does not resinify.

4. Derivatives of the preceding Monobasic Acids.—The hydrogen atoms of the radicals in these acid hydrates are replaceable by halogen atoms, by the nitro group (NO_2), the amido group (NH_2), the cyanogen group (CN), etc. These substituted acids do not lose their character as acid hydrates, but may form corresponding salts and esters. A few of the most important of these derivatives will be noted.

Chloracetic Acids.—Monochloracetic, Dichloracetic, and Trichloracetic acids are all known, the formulas being $CH_2Cl.COOH$, $CHCl_2.COOH$, and $CCl_3.COOH$. Trichloracetic acid is readily formed by the oxidation with nitric acid of the corresponding aldehyde, chloral. It decomposes easily, the aqueous solution even on boiling, into chloroform and carbon dioxide. It is a powerful caustic, and has been used in medicine for this purpose. It precipitates albumen solutions quantitatively, does not affect albumen peptones, but precipitates gelatin peptones and gelatin solutions. It is adapted for the quantitative determination of albumen.

The nitro-fatty acids are of no special importance. With tin and hydrochloric acid they yield the corresponding amido-fatty acids. The amido-fatty acids are more important, because they are among the commonest of the decomposition products of the albuminoids.

Amido-formic Acid, NH_2COOH. (See Carbamic Acid, under Carbonyl Compounds.)

Amido-acetic Acid, $CH_2(NH_2).COOH$.—This important substance, known also as "glycocoll," is readily obtained by boiling

glue or silk with alkalies or acids, by the decomposition of hippuric acid (see p. 772) with hydrochloric acid, or by heating monochloracetic acid with ammonia. It forms large, colorless, rhombic prisms, easily soluble in water, insoluble in absolute alcohol and ether; melts with decomposition at 232° to 236°. As an amido-acid it unites in itself both the properties of a base and an acid. It forms a hydrochlorate on the one hand, and a well-crystallized copper salt on the other. Substitution derivatives from glycocoll are also obtained by the replacement of the hydrogen of the amido group. Thus, from glycocoll, $\begin{matrix}CH_2.NH_2\\|\\COOH\end{matrix}$, we obtain methyl-glycocoll, or *sarcosine*, $\begin{matrix}CH_2.NH(CH_3)\\|\\COOH\end{matrix}$, which is a decomposition product of creatine and caffeine (see p. 719), and trimethyl-glycocoll, or *betaïne*, $\begin{matrix}CH_2.N(CH_3)_3\\|\\CO.O\end{matrix}$, which is contained in beet-root and cotton-seed, and is related to choline.

Amido-propionic Acid, $CH_3.CH(NH_2).COOH$, is also known as "alanine." It can be obtained by the action of dilute acids upon silk or the action of hydrocyanic acid upon aldehyde-ammonia. Hard needles of sweetish taste.

Amido-butyric Acid, $NH_2.(CH_2)_3.COOH$.—One of the amido-butyric acids is piperidinic acid, which results from the oxidation of piperyl-urethan.

Amido-valeric Acid, $NH_2(CH_2)_4.COOH$.—One of the amido-valeric acids has been obtained in the decomposition of fibrin and flesh, and of conine and piperidine derivatives, and has also been found in the pancreas of the ox.

Amido-caproic Acid, $C_5H_{10}(NH_2)COOH$. — This important substance is known also as "leucine," and is found widely spread in both animal and vegetable material. It is found in old cheese, in the animal organism in the gastric salivary gland, and along with tyrosine is a constant product of the digestion of albumen in the small intestine and of the decay of albuminous substances; it is also found in the shoots of the vetch and the gourd. Most conveniently made by boiling clippings of horn with dilute sulphuric acid. Forms scales soluble in water, difficultly soluble in cold, more readily soluble in hot alcohol. Leucine is dextro-rotatory, but is made inactive by heating with baryta water.

5. Acids derived from Diatomic Alcohols.—The diatomic alcohols or glycols have, it will be recalled, two alcoholic hydroxyl groups or act like diacid bases. If these two hydroxyl groups are both attached so as to furnish the primary alcohol group, $CH_2.OH$, we may obtain by oxidation two groups, COOH, characteristic of organic acids. At the same time one alcoholic group may be oxidized, while the other remains unchanged. Thus, we obtain from diatomic alcohols two series of acids: one series, diatomic but monobasic, compounds which are half alcohol and half acid; and a second series, diatomic and dibasic compounds, which are purely acid in character.

TABLE OF THE ACIDS DERIVED FROM DIATOMIC ALCOHOLS.

Diatomic Alcohol. General Formula, $C_nH_{2n+2}O_2$.	Monobasic Alcohol-Acid. Formula, $C_nH_{2n}O_3$.	Dibasic Acid. Formula, $C_nH_{2n-2}O_4$.
Ethylene glycol, $\begin{matrix}CH_2OH\\ \vert\\ CH_2OH.\end{matrix}$	Glycollic acid, $\begin{matrix}CH_2OH\\ \vert\\ COOH.\end{matrix}$	Oxalic acid, $\begin{matrix}COOH\\ \vert\\ CO.OH.\end{matrix}$
Propylene glycol, $\begin{matrix}CH_2OH\\ \vert\\ CH_2\\ \vert\\ CH_2OH.\end{matrix}$	Lactic acid, $\begin{matrix}C_2H_4.OH\\ \vert\\ COOH.\end{matrix}$	Malonic acid, $\begin{matrix}COOH\\ \vert\\ CH_2\\ \vert\\ COOH.\end{matrix}$
Butylene glycol, $\begin{matrix}CH_2OH\\ \vert\\ C_2H_4\\ \vert\\ CH_2OH.\end{matrix}$	Oxybutyric acid, $\begin{matrix}C_3H_6.OH\\ \vert\\ COOH.\end{matrix}$	Succinic acid, $\begin{matrix}COOH\\ \vert\\ C_2H_4\\ \vert\\ COOH.\end{matrix}$
Amylene glycol, $\begin{matrix}CH_2OH\\ \vert\\ C_3H_6\\ \vert\\ CH_2OH.\end{matrix}$	Oxyvaleric acid, $\begin{matrix}C_4H_8.OH\\ \vert\\ COOH.\end{matrix}$	Pyrotartaric acid, $\begin{matrix}COOH\\ \vert\\ C_3H_6\\ \vert\\ COOH.\end{matrix}$

The alcohol acids are obtained by the regulated oxidation of the glycols, or by the action of moist silver oxide or water alone upon the monochlor derivatives of the fatty acids. Thus, glycollic acid is derived from monochloracetic acid: $CH_2Cl.COOH + H_2O = CH_2(OH).COOH + HCl$.

Glycollic Acid, $CH_2OH.COOH$, is found in unripe grapes and in the leaves of the wild vine. Forms colorless needles, melting at 78°–79°. Easily soluble in water, alcohol, and ether.

Lactic Acid, $C_2H_4.OH.COOH$.—Two isomeric acids are indicated by theory: Ethylidene-lactic acid, $CH_3.CH(OH).COOH$, and ethylene-lactic acid, $CH_2OH.CH_2.COOH$. Of the first of these, however, there are two physical isomers, the optically

inactive ethylidene-lactic acid (lactic acid of fermentation) and the active ethylidene-lactic acid (sarco-lactic acid).

Fermentation lactic acid (**Acidum Lacticum,** U. S. P.) occurs in opium, sauerkraut, the gastric juice, and the gray matter of the brain. It is produced by the lactic fermentation of sugar (see p. 708), and hence contained in such products as sour milk, koumiss, kefir, etc. The official lactic acid contains 75 per cent. of absolute lactic acid, and is a colorless, syrupy liquid, odorless, of acid taste, and sp. gr. about 1.213 at 15°. It is hygroscopic, and freely miscible with water, alcohol, or ether; insoluble in chloroform, benzine, or carbon disulphide. Lactic acid when heated in dry air gives rise to characteristic anhydrides. Thus, $2C_3H_6O_3 - H_2O = C_6H_{10}O_5$, *Lactic Anhydride*, and this at a higher temperature again loses a molecule of water, yielding *Lactide*, $C_6H_8O_4$, a stable compound crystallizing in colorless tablets, melting at 125°, and boiling undecomposed at 255°. The official metallic lactates are:

Ferri Lactas, U. S. P., $Fe(C_3H_5O_3)_2 + 3H_2O$. — This salt is in pale, greenish-white crusts or needle-shaped crystals, with a slight, peculiar odor, and a mild, sweetish, ferruginous taste. Slowly but completely soluble in water, almost insoluble in alcohol, freely soluble in solutions of alkaline citrate.

Strontii Lactas, U. S. P., $Sr(C_3H_5O_3)_2 + 3H_2O$.—A white, granular or crystalline compound, odorless, and of a slightly bitter, saline taste. Permanent in air. Soluble in water and alcohol.

Sarco-lactic (or Para-lactic) acid is found in the muscles (hence also in extract of beef), in the blood, and in the urine after strong muscular exertion. It is the dextro-rotatory modification, and can be produced together with the lævo-rotatory modification by splitting up the inactive or ordinary lactic acid. This is accomplished by the fractional crystallization of the strychnine salt.

Ethylene-lactic (or Hydracrylic) acid forms a syrupy mass. It differs from ordinary lactic acid in yielding carbonic and oxalic acids on oxidation instead of acetic acid, and in not yielding an anhydride on heating, but breaking up into water and acrylic acid, whence the name hydracrylic.

Oxybutyric Acid, $C_3H_6OH.COOH$. — An optically active (lævo-rotatory) modification of this acid is found in the urine and the blood of diabetic patients.

The dibasic acids result when the diatomic alcohols are oxidized with nitric acid or by the saponification of the cyanogen derivative of the fatty acids.

Oxalic Acid, COOH.COOH, occurs in many plants, as in wood-sorrel (*Oxalis acetosella*), in the form of KHC_2O_4, in the varieties of Rumex, as $Na_2C_2O_4$ in varieties of *Salicornia*, and as CaC_2O_4 in rhubarb, beets, etc. It may be formed by the oxidation of sugar, starch, etc., with nitric acid, or by fusing cellulose with hydrate of potash and soda, the latter method being employed on a large scale. It crystallizes with $2H_2O$, is soluble in water, more difficultly soluble in alcohol, almost insoluble in ether. Decomposes on strong heating, or in the presence of dehydrating agents like sulphuric acid, according to the reaction :

$$COOH—COOH = CO_2 + CO + H_2O.$$

When heated with glycerin, formic acid is produced.

Forms monoclinic prisms, which effloresce in dry air. Is used extensively in calico printing as a mordant, as a solvent for iron stains, and in the analytical laboratory as a reagent for lime. But a single metallic oxalate is now official :

Cerii Oxalas, U. S. P., $Ce_2(C_2O_4)_3+9H_2O$.—It forms a white, granular powder, without odor or taste, permanent in air. Insoluble in water, alcohol, ether, or solutions of potassium or sodium hydrate, soluble in diluted sulphuric or hydrochloric acids.

The calcium salt is insoluble, and at times occurs in urinary concretions ; the double potassio-ferrous oxalate has a powerful reducing action on silver and platinum salts, and is used in photography as a developing solution.

Malonic Acid, $COOH.CH_2.COOH$, occurs in beet-root, and may be produced from malic acid by oxidation with chromic acid, whence the name. It forms large plates readily soluble in water, alcohol, and ether, melting at 133°–134°.

Succinic Acid, $COOH.C_2H_4.COOH$, is found in amber, in various resins and lignite, in the poppy, in unripe grapes, and in urine and blood. It may be obtained by the oxidation of the higher fatty acids, the fats, and waxes with nitric acid, from gums and sugars by fusing with caustic potash, and as a side-product in the alcoholic fermentation of sugar. It is usually obtained by distilling amber or by the fermentation of a solution of tartrate of ammonia. It crystallizes in prisms or tablets, fuses at 182°, and boils at 235°, yielding, however, the anhydride. It is soluble in water and ether, more difficultly in alcohol. The most important salt is the basic ferric succinate, which is insoluble, and by means of which iron is sometimes separated qualitatively from other metals.

Pyrotartaric Acid, $COOH.C_3H_6.COOH$.—Of the several isomeric forms, the most important are glutaric acid, the normal pyrotartaric acid, which is found in suint of sheep's wool and in juice of the beet-root, and methyl-succinic acid.

Of the higher acids of this series may be mentioned *Adipic Acid*, $(CH_2)_4.(COOH)_2$, obtained by the oxidation of the fats by nitric acid; *Suberic Acid*, $C_8H_{14}O_4$, obtained by the action of nitric acid upon cork tissue; *Sebacic Acid*, $C_{10}H_{18}O_4$, obtained by the dry distillation of spermaceti and fats containing oleic acid; and *Roccllic Acid*, $C_{17}H_{32}O_4$, found in the lichen *Rocella fuciformis*.

From unsaturated alcohols containing two $CH_2.OH$ groups may also be prepared acids which will, of course, show the unsaturated character. They bear to the acids just described the same relation that the oleic acid series does to the fatty acid series. They have the general formula $C_nH_{2n-4}O_4$. The most important are:

Fumaric and *Maleic Acids*, $C_2H_2(COOH)_2$.—The first of these isomeric acids is found in *Fumaria officinalis*, in mushrooms, and in Iceland moss. It is formed from malic acid by the loss of water, and from albuminoids by the action of aqua regia. Under the influence of nascent hydrogen, it takes up two H atoms and yields succinic acid. When heated strongly for a time it changes into the isomeric maleic acid. This acid may also be obtained by the distillation of malic acid. It is more soluble in water than fumaric acid.

6. Acids derived from Triatomic and Higher Alcohols.—No matter what the number of OH groups contained in the alcohols, whether three, as in the glycerins, or four, five, or six, the presence of a group, CH_2OH, gives rise to the acid character in the products of oxidation, and the basicity of the acid depends upon the number of the $CH_2.OH$ groups so changed to COOH.

Glyceric Acid, $CH_2OH.CHOH.COOH$, results from the careful oxidation of glycerin with nitric acid, and is obtained also in the spontaneous decomposition of nitroglycerin. Syrup, soluble in water and alcohol.

Tartronic Acid, $COOH.CHOH.COOH$, results from the oxidation of glycerin with potassium permanganate. Prismatic crystals easily soluble in water and alcohol, difficultly soluble in ether. Melting point 185°.

Malic Acid, $COOH.CH_2.CHOH.COOH$, known also as oxysuccinic acid, is very widely distributed in the vegetable king-

TABLE OF ACIDS DERIVED FROM HIGHER ALCOHOLS.

Alcohols.	Monobasic Acids.	Dibasic Acids.	Tribasic Acids.
Triatomic: Glycerin, $CH_2OH.CHOH.CH_2OH$	Glyceric, $CH_2OH.CHOH.COOH$	Tartronic, $COOH.CHOH.COOH$ Malic, $CH_2.CHOH(COOH)_2$	Tricarballyic, $C_3H_5.(COOH)_3$ Aconitic, $C_3H_3(COOH)_3$
Tetratomic: Erythrite, $C_4H_6(OH)_4$	Erythritic, $C_3H_4(OH)_3COOH$	Tartaric, $C_2H_2(OH)_2(COOH)_2$	Citric, $C_3H_4(OH)(COOH)_3$
Pentatomic: Arabite, Xylite, $C_5H_7(OH)_5$ Rhamnite, $C_6H_9(OH)_5$	Arabonic, Xylonic, $C_4H_5(OH)_4COOH$ Rhamnonic, $C_5H_7(OH)_4COOH$ Saccharinic, $C_5H_7(OH)_4COOH$	Trioxyglutaric, Aposorbic, $(CHOH)_3(COOH)_2$	Oxycitric, $C_3H_3(OH)_2(COOH)_3$
Hexatomic: Mannite, $C_6H_8(OH)_6$ Dulcite, $C_6H_8(OH)_6$	Mannitic, Gluconic, Gulonic, $C_5H_6(OH)_5.COOH$ Galactonic, Talonic, $C_5H_6(OH_5)(COOH)_2$	Saccharic, $C_4H_4(OH)_4(COOH)_2$ Mucic, $C_4H_4(OH)_4(COOH)_2$	

Both monobasic and dibasic heptonic, octonic, and nonnonic acids have also been obtained in connection with the synthetic work of Emil Fischer upon the sugars. They are as yet of theoretical interest only.

dom, being found in unripe apples, quinces, grapes, barberries, etc. It may be formed also from succinic acid, on the one hand, by replacing an H atom by OH, or from tartaric acid, on the other hand, by reduction with HI.

It forms hygroscopic needles, easily soluble in water and alcohol, only slightly soluble in ether. Melting point 100°. Heated to 120°–130 it yields fumaric acid, and at 175°–180° malic acid is formed.

The amides and amines of malic acid will be considered farther on.

Tricarballylic Acid, $C_3H_5.(COOH)_3$, occurs in unripe beets, and is prepared synthetically from glycerin through the intervention of the bromine and cyanogen compounds of the glyceryl radical, C_3H_5. Its relations to citric and aconitic acids are seen from the table, and it can be formed from both by simple reactions. It forms prisms, melting at 166°, soluble in water.

Aconitic Acid, $C_3H_3(COOH)_3$, is an unsaturated acid. It is found in nature in *Aconitum napellus*, *Achillea millefolium*, in the sugar-cane, and the beet-root. It is also readily prepared by quick heating of citric acid, when a molecule of H_2O separates. It forms crystals, melting at 186°. Easily soluble in water.

Erythritic Acid, $C_3H_4(OH)COOH$, is formed by the oxidation of erythrite with nitric acid or platinum black.

Tartaric Acid, COOH.CHOH.CH.OH.COOH (**Acidum Tartaricum**, U. S. P.), is sometimes known also as dioxy-succinic or oxy-malic acid, in order to indicate its relations to these well-known acids. Tartaric acid exists in four *physically isomeric* modifications: dextro-tartaric, lævo-tartaric, racemic or inactive tartaric, and meso-tartaric. The first of these is the naturally occurring variety. It occurs partly free and partly as potassium or lime-salt in the juice of the grape and other fruits. The acid potassium tartrate which is found in the grape juice becomes insoluble as fermentation proceeds, and the liquid becomes alcoholic and separates as "argols" in the wine-casks. This is purified by conversion into the lime-salt from which the acid is liberated with H_2SO_4. The pure acid forms colorless, monoclinic prisms or white powder, with an acid taste, and permanent in the air. Is soluble in water and alcohol, difficultly soluble in ether, nearly insoluble in chloroform, benzene, or benzine. Melting point 135°. It reduces an ammoniacal silver solution upon warming. When strongly heated, carbonizes and gives off a characteristic "caramel" odor. The most important tartrates are:

Neutral Potassium Tartrate, $K_2C_4H_4O_6+\frac{1}{2}H_2O$, which forms monoclinic prisms easily soluble in water.

Acid Potassium Tartrate, $KHC_4H_4O_6$, or **Potassii Bitartras, U. S. P.**—This compound, known also as "cream of tartar," forms small rhombic crystals, odorless, and having a pleasant acidulous taste, sparingly soluble in cold water and in alcohol.

Potassii et Sodii Tartras, U. S. P., $KNaC_4H_4O_6+4H_2O$.—This compound, known also as Rochelle or Seignette salt, forms large, colorless, rhombic prisms, odorless, and with a cool, saline taste. The crystals effloresce slightly in dry air. Soluble in water, almost insoluble in alcohol.

Antimonii et Potassii Tartras, U. S. P., $2K(SbO)C_4H_4O_6+H_2O$.—This compound, known also as "tartar emetic," forms colorless, transparent crystals, becoming opaque and white on exposure to the air. Soluble in water, but insoluble in alcohol. It is poisonous and acts as an emetic, and is used as a mordant in dyeing.

Ferri et Ammonii Tartras, U. S. P., and **Ferri et Potassii Tartras, U. S. P.**, are uncrystallizable double salts, which are obtained as syrupy solutions and dried in films, which are then broken up, and constitute what are called "scale preparations."

The *Lævo-tartaric Acid* is like the dextro-tartaric in its chemical properties, but is the opposite in its behavior towards polarized light. When equal quantities of both acids are mixed together in aqueous solution, the solution becomes warm, and we obtain

Racemic Acid, $C_4H_6O_6+H_2O$.—Racemic acid is found sometimes in grape juice, and in the mother liquor from the crystallization of tartar. Its crystals are rhombic, efflorescent, and less soluble than those of dextro-tartaric acid. It is optically inactive. Its salts are called racemates. When the sodium-ammonium salt is crystallized from solution, the crystals obtained show hemihedral faces (*i.e.*, only one-half the faces of the normal figure are developed). Pasteur first observed that these crystals differed, part being dextro-hemihedral, and part being lævo-hemihedral, and that the lævo-hemihedral crystals were dextro-rotatory in solution, and *vice versa*. If, then, the two kinds of crystals are separated from each other mechanically, and the free acid liberated from each, it is found that we have no racemic acid remaining; but in the one case have dextro-tartaric, and in the other case lævo-tartaric acid.

If to a solution of ammonium racemate be added the ferment *Penicillium glaucum*, the dextro-tartaric acid is decomposed faster than the lævo-tartaric, and the latter may thus be obtained.

Meso-tartaric Acid is also an inactive variety, but is not decomposable like racemic acid into active modifications. It is produced along with racemic acid in different reactions. Forms efflorescent plates, fusing at 146°.

Citric Acid, $C_3H_4(OH)(COOH)_3$ (**Acidum Citricum**, U. S. P.).—This important acid occurs in the free state in lemons, oranges, etc., and, mixed with malic acid, in gooseberries, currants, and mulberries, and, as calcium salt, in wood, potatoes, beet-root, etc. Is prepared generally from lemon juice, which contains 6 to 7 per cent. of the acid. The acid is separated in the form of the difficultly soluble lime-salt ; this is decomposed by sulphuric acid, and the acid solution concentrated in vacuo to the point of crystallization. A new source of citric acid manufacture has been recently announced, which may prove to be more economical than the extraction from lemon juice. Dr. Carl Wehmer has discovered that sugar solutions exposed to the action of certain microscopic fungi, the spores of which are present in the atmosphere, become transformed into citric acid. It is claimed that 11 kilogrammes of sugar treated in this way have yielded 6 kilogrammes of crystallized citric acid. The acid crystallizes with one molecule of water in colorless, rhombic prisms, which are odorless, and have an agreeable acid taste ; effloresce in warm air, and deliquesce when exposed to moist air. Is soluble in water and alcohol, slightly soluble in ether. When heated to 135° it loses its water of crystallization, melts at 153°, and breaks up at a higher temperature into aconitic acid and water, and then into itaconic acid and CO_2.

The official metallic citrates are :

Potassii Citras, U. S. P., $K_3C_6H_5O_7+H_2O$.—Forms colorless crystals or white granular powder, odorless, and with a cooling, saline taste.

Lithii Citras, U. S. P., $Li_3C_6H_5O_7$.—Forms a white powder, odorless, with a cooling, faintly alkaline taste, deliquescent on exposure to air.

Bismuthi Citras, U. S. P., $BiC_6H_5O_7$. — Forms a white amorphous or faintly crystalline powder, odorless, tasteless, and permanent in air.

Besides these crystalline salts, we have as evaporated syrups or "scale preparations :" **Bismuthi et Ammonii Citras**,

U. S. P., **Ferri Citras,** U. S. P., and **Ferri et Ammonii Citras,** U. S. P. The magnesium citrate is also official in **Liquor Magnesii Citratis,** U. S. P., and **Magnesii Citras Effervescens,** U. S. P.

The monobasic pentatomic acids, *arabonic*, *xylonic*, *rhamnonic*, and *saccharinic* acids, are obtained by the oxidation of the corresponding pentose sugars. They possess only a theoretical interest.

Oxycitric Acid, $C_3H_3(OH)_2(COOH)_3$, is found in beet and turnip juice, and has been prepared artificially from aconitic acid.

The monobasic and dibasic hexatomic acids are obtainable both from the hexatomic alcohols mannite and dulcite and from the sugars related to them. The dibasic acids especially are produced from a variety of sources among the class of carbohydrates.

Saccharic Acid, $(CHOH)_4(COOH)_2$, is produced by the oxidation of cane-sugar, dextrose, mannite, or starch by nitric acid. Brittle, very hygroscopic mass, easily soluble in water. The ammonium salt of saccharic acid is decomposed at 160° into pyrrol, ammonia, and carbon dioxide : $C_6H_8(NH_4)_2O_8 = C_4H_5N + 2CO_2 + NH_3 + 4H_2O$.

Mucic Acid, $(CHOH)_4.(COOH)_2$, is obtained by the oxidation of milk-sugar, gums, and mucilages by nitric acid. White crystals, fusing at 213°, difficultly soluble in water. The ammonium salt decomposes like the corresponding salt of saccharic acid into pyrrol, carbon dioxide, and ammonia.

7. Aldehydic and Ketonic Acids.—Mention was made under the oxidation products of diatomic alcohols of alcohol acids. It is obvious that another intermediate class may be aldehyde acids, and where secondary alcohol groups exist, combined in the same molecule with primary alcoholic groups, we may obtain ketonic acids, or acids in which we have both the ketone group, CO, and the carboxyl group, COOH.

Glyoxalic Acid, CHO.COOH, is an aldehyde acid found in unripe fruits, such as grapes, gooseberries, etc. It crystallizes in prisms, easily soluble in water.

Glycuronic Acid, $COH.(CHOH)_4.COOH$, is an aldehydic acid obtained by the reduction of saccharic acid. It also possesses interest as being found in the urine as a decomposition product after taking internally such substances as camphor, phenol, phenetol, α- and β-naphthol.

Pyroracemic Acid, $CH_3.CO.COOH$ (aceto-formic acid), is a ketone acid resulting from the dry distillation of tartaric, racemic,

and glyceric acids. It is a colorless liquid, soluble in water, alcohol, and ether, boiling with slight decomposition at 165°–170°, and smelling of acetic acid and extract of beef.

Aceto-Acetic Acid, $CH_3.CO.CH_2COOH$, is a strongly acid liquid miscible with water, and breaking up upon warming into acetone and carbon dioxide. Its ethyl ester is obtained in the form of its sodium compound by the action of sodium upon ethyl acetate, and from the ester the free acid is obtained by saponification.

Levulinic Acid, $CH_3.CO.CH_2.CH_2COOH$ (aceto-propionic acid), results from the action of acids upon cane-sugar, lævulose, cellulose, gum, starch, and other carbohydrates. A condensation product of levulinic acid with phenyl-hydrazine is known in medicine under the name of "antithermin."

VII. Esters, or Ethereal Salts.

These are bodies formed by the replacement of the hydrogen of an acid, whether inorganic or organic, by an alcohol radical as base. They are, as stated, ethereal salts, and may include acid, neutral, and basic salts, or esters, as more generally termed.

1. Esters of Inorganic Acids.—The esters of the haloid acids have already been described as the halogen derivatives of the hydrocarbons.

The esters of nitrous acid are obtained by passing nitrous fumes into the alcohols, or by the action of copper and nitric acid upon the same. They are liquids of aromatic odor, and very low boiling points, and are easily saponifiable. Nascent hydrogen reconverts them into alcohol, ammonia being formed at the same time.

Methyl Nitrite, CH_3ONO, is gaseous at ordinary temperatures.

Ethyl Nitrite, $C_2H_5O.NO$, is a mobile liquid of penetrating ethereal odor and peculiar stinging taste. Boils at 18°, and burns with a bright white flame. Its alcoholic solution is the **Spiritus Ætheris Nitrosi**, U. S. P., known also as "sweet spirit of nitre." This is stated by the U. S. Pharmacopœia to be "an alcoholic solution of ethyl nitrite yielding, when freshly prepared and tested in a nitrometer, not less than 11 times its own volume of nitrogen dioxide." The official spirit is 22 times the weight of the ethyl nitrite contained. It is now made by the action of sulphuric acid upon a mixture of sodium nitrite and alcohol.

Iso-Amyl Nitrite, $C_5H_{11}O.NO$ (**Amyl Nitris**, U. S. P.), is obtained by the action of nitrous acid upon iso-amyl alcohol. Forms a clear, yellow or pale yellow liquid, of peculiar, ethereal, fruity odor, and pungent, aromatic taste. Almost insoluble in water, soluble in alcohol and ether. Sp. gr. 0.87 to 0.88. Boils at 97° to 98°, yielding an orange-colored vapor. It is used in medicine, producing expansion of the blood-vessels and relaxation of the contractile muscles.

Isomeric with the nitrites of the alcoholic radicals are the nitro-derivatives of the hydrocarbons, which are formed by the action of metallic nitrites upon the halogen derivatives of the hydrocarbons. Thus, nitro-ethane, $C_2H_5.NO_2$, is isomeric with ethyl nitrite, $C_2H_5O.NO$.

The esters of nitric acid are obtained by the action of nitric acid upon the alcohols. However, as nitric acid tends to have an oxidizing action upon the alcohols, whereby nitrous acid is formed and in consequence the nitrous esters, urea is added, which decomposes the nitrous acid as formed and nitric esters are the sole product.

Methyl Nitrate, $CH_3.NO_3$, is a colorless liquid, boiling at 66°. Its vapor heated above the boiling point decomposes with explosive violence.

Ethyl Nitrate, $C_2H_5.NO_3$, is a mobile liquid of agreeable odor and sweet taste, but with bitter after-taste. It burns with a white flame. Boiling point 86°. Its vapor is also explosive when heated.

Glycollic Dinitrate, $C_2H_4(NO_3)_2$, is prepared by acting on glycol with sulphuric and nitric acids. It is a yellowish liquid, insoluble in water, which is saponified by alkalies, and explodes on being heated.

Glyceryl Trinitrate, $C_3H_5(NO_3)_3$.—This important compound, commonly known as "nitroglycerin," is formed by the action of a cold mixture of concentrated nitric and sulphuric acids upon glycerin. It is a colorless or slightly yellowish oil, insoluble in water, soluble in alcohol and ether. It has a sweet, burning, aromatic taste, and is poisonous. It crystallizes at —20° in needles. It burns without explosion when in a thin film, but when quickly heated or struck explodes with terrible violence. When mixed with infusorial earth in the proportion of 3 parts to 1, it forms dynamite, which is not affected so readily by simple percussion, but is exploded by fulminate of mercury with great force. Nitroglycerin is saponified by alkalies and by sulphide of ammonium.

A one-per-cent. alcoholic solution of nitroglycerin constitutes the **Spiritus Glonoini, U. S. P.**

Nitro-erythrite, $C_4H_6(NO_3)_4$, and *Nitro-mannite*, $C_6H_8(NO_3)_6$, are similar esters of nitric acid, and are like nitroglycerin in explosive characters, although less violent.

The esters of sulphuric acid are formed by the action of sulphuric acid upon the alcohols. As sulphuric acid is dibasic, two series of esters are possible, just as acid and neutral sulphates of inorganic bases are formed.

Acid Ethyl Sulphate (or Ethyl-sulphuric Acid), $C_2H_5HSO_4$, is obtained on mixing equal parts of absolute alcohol and concentrated sulphuric acid. The free acid is a syrup easily soluble in water. Under the old name of "sulpho-vinic acid," it has long been known as the intermediate product in the "continuous ether process" (see p. 638). Its salts, formerly called "sulphovinates," crystallize well. They are, of course, double sulphates of ethyl and metallic base.

Neutral Ethyl Sulphate, $(C_2H_5)_2SO_4$, is a colorless, oily liquid, insoluble in water, of a pleasant peppermint odor. It boils at 208°. The corresponding esters of sulphurous acid are known, but are prepared with more difficulty, as the isomeric sulphonic acid derivatives (see p. 641) tend to form by the reaction with metallic sulphites.

The esters of phosphoric, silicic, and carbonic acids are also known. The last of these will be referred to later. (See Carbonyl Derivatives.)

2. Esters of Organic Acids.—These form in some cases by the direct action of the acids upon the alcohols, but more generally it is necessary to provide for taking up the water which forms in the reaction. This is done by the addition of sulphuric acid as dehydrating agent to the mixture of alcohol and organic acid, or still more readily by passing dry HCl gas into a mixture of the alcohol and acid. This probably acts by first forming an acid chloride with the radical of the organic acid, and this then reacts with the alcohol.

The esters of the lower members of the fatty acid series are for the most part colorless, neutral liquids, which volatilize without decomposition. As a rule they are insoluble in water, but soluble in alcohol and ether. The esters of the higher acids are solids, and play an important part in nature as the natural fats and waxes.

The esters are, without exception, saponifiable; that is, under the influence of water or alkalies and acids they break up into the

free alcohol and acid, or alkaline salt of the acid, in case alkalies are used for the saponification.

Ethyl Formate, $HCO.OC_2H_5$.—Boils at 55°. Is employed in the manufacture of artificial rum or arrack, as well as in peach essence and other fruit essences.

Ethyl Acetate, $C_2H_3O.OC_2H_5$ (**Æther Aceticus**, U. S. P.). Boils at 77.5° ; is a transparent, colorless liquid of fragrant and refreshing odor and a peculiar acetous and burning taste ; is moderately soluble in water, easily soluble in all proportions in alcohol, ether, fixed and volatile oils. It is inflammable, burning with a yellowish flame and acetous odor. Besides being used internally in medicine, it is largely used in admixture in fruit essences and as a solvent.

Amyl Acetate, $C_2H_3O.OC_5H_{11}$.—Boiling point 138°. This ester has a characteristic fragrant odor of pears, and hence is the basis of the artificial pear essence. It is also used largely as an ingredient in the manufacture of pyroxylic varnishes, owing to its solvent power.

Octyl Acetate, $C_2H_3O.OC_8H_{17}$.—Boiling point 210°. Forms the chief constituent of the oil from the fruit of *Heracleum spondylium*.

Ethyl Butyrate, $C_4H_7O.OC_2H_5$.—Boiling point 120.9° ; possesses the characteristic odor of pineapples, and hence is used in that fruit essence.

Iso-amyl Butyrate, $C_4H_7O.OC_5H_{11}$.—Boiling point 178.6°. Is also used in the manufacture of pineapple essence

Ethyl Iso-valerate, $C_5H_9O.OC_2H_5$.—Boiling point 134.3°. Is a constituent of melon and peach oils.

Iso-amyl Iso-valerate, $C_5H_9O.OC_5H_{11}$.—Boiling point 196°. Is the chief constituent of apple essence.

Iso-amyl Caprinate, $C_{10}H_{19}O.OC_5H_{11}$.—Boiling point 275°, with partial decomposition. This is the chief constituent of wine fusel oil, and under the misapplied name of "œnanthic ether," gives the bouquet to wine.

Cetyl Palmitate, $C_{16}H_{31}O.OC_{16}H_{33}$.—Fusing point 53.5°. This ester forms the chief constituent of spermaceti (**Cetaceum**, U. S. P.), a peculiar, fatty solid obtained from the head of the sperm whale (*Physeter macrocephalus*). This solid ester is held dissolved in the sperm oil during the life of the animal, and after death, with the disappearance of the animal heat, it crystallizes out. It forms a white, somewhat translucent, slightly unctuous mass, of a scaly, crystalline fracture and pearly lustre ; odorless,

and with a bland, mild taste. Sp. gr. about 0.945 at 15°. It is insoluble in water, and nearly so in cold alcohol; soluble in boiling alcohol, also in ether, chloroform, carbon disulphide, fixed and volatile oils.

Ceryl Palmitate, $C_{16}H_{31}O.OC_{27}H_{55}$.—Fusing point 79°. Is the chief constituent of opium wax.

Myricyl Palmitate, $C_{16}H_{31}O.OC_{30}H_{61}$.—Fusing point 72°. Is the part of beeswax insoluble in alcohol, the soluble part consisting largely of cerotic acid (see p. 654). Beeswax (**Cera Flava**, U. S. P.) is an animal product, being the material of the cell walls of the combs of the *Apis mellifica*, or honey bee. It is a yellowish to brownish-yellow solid, having an agreeable, honey-like odor, and a faint, balsamic taste. Sp. gr. 0.955 to 0.967 at 15°; melting point 63°–64°. It is insoluble in water, sparingly soluble in cold alcohol, but almost completely soluble in boiling alcohol. It is completely soluble in ether, chloroform, and fixed and volatile oils.

Beeswax is bleached white to adapt it for use in candle-making and other purposes. This is accomplished either by the action of light and air (air-bleached wax), or by the use of oxidizing agents, such as potassium dichromate, potassium permanganate, and hydrogen dioxide (chemically-bleached wax). The product is a yellowish-white solid (**Cera Alba**, U. S. P.), which is slightly more crystalline than the yellow wax, and contains rather more free acid.

Ceryl Cerotate, $C_{27}H_{53}O.OC_{27}H_{55}$.—Fusing point 82°. Forms the chief ingredient of Chinese insect wax. It is also found in opium wax.

Myricyl Cerotate, $C_{27}H_{53}O.OC_{30}H_{61}$, is found in carnauba wax.

Probably the most important of the esters of organic acids, however, are the compounds of the triatomic alcohol glycerin. The esters of this alcohol with the members of the fatty acid series make up the bulk of the vegetable and animal fats and fatty oils. While glycerin as a triacid base can form esters containing one, two, or three molecules of fatty acid, we find that the naturally occurring compounds are exclusively neutral esters,—that is, contain three molecules of the monobasic acid in combination with the base. The mono-acid and di-acid compounds can be formed artificially, however, in many cases.

The most important of the glycerin esters are:

Monoformin, $C_3H_5(OH)_2OCHO$, and *Diformin*, $C_3H_5(OH)(OCHO)_2$, have been obtained artificially; the former by heating

glycerin with oxalic acid to 190°, and the latter as a side-product in the manufacture of formic acid by the action of oxalic acid on glycerin at 140°.

Monoacetin, $C_3H_5(OH)_2OC_2H_3O$, and *Diacetin*, $C_3H_5(OH)(OC_2H_3O)_2$, are both obtained by the prolonged action of glacial acetic acid upon glycerin under pressure. They are liquids of high boiling point.

Triacetin, $C_3H_5(OC_2H_3O)_3$, is found naturally in certain fats, as in the oils from the seeds of *Euonymus europæus*. Is also made artificially by the action of glacial acetic acid upon glycerin in the presence of anhydrous sodium acetate.

Tributyrin, $C_3H_5(OC_4H_7O)_3$, can be made from glycerin and normal butyric acid. Is found naturally in milk fat, and hence in butter, to which it gives an agreeable taste and odor. Mass of buttery consistence, boiling at 285°. Decomposes spontaneously in presence of air and moisture into butyric acid and glycerin.

Tri-isovalerin, $C_3H_5(OC_5H_9O)_3$, is found in dolphin oil.

Tricapronin, $C_3H_5(OC_6H_{11}O)_3$.—The glyceride of isobutyl-acetic acid, $C_6H_{12}O_2$, is found in cow's butter, goat's milk, and in cocoanut oil.

Tricaprylin, $C_3H_5(OC_8H_{15}O)_3$.—The glyceride of the normal caprylic acid is also found in cow's butter, goat's milk, and in cocoanut oil.

Tricaprin, $C_3H_5(OC_{10}H_{19}O)_3$.—The glyceride of this acid is found in goat's milk and in cocoanut oil.

Trilaurin, $C_3H_5(OC_{12}H_{23}O)_3$, forms crystalline needles, melting at 45°. This glyceride forms the chief constituent of cocoanut oil, and is found also in palm-nut oil and bayberry oil.

Trimyristin, $C_3H_5(OC_{14}H_{27}O)_3$, forms crystalline plates, melting at 55°. Is found in nutmeg butter, in palm-nut oil, cocoanut oil, goose fat, and cow's butter.

Tripalmitin, $C_3H_5(OC_{16}H_{31}O)_3$, forms indistinct crystals, fusing at 62°. Insoluble in water and alcohol, easily soluble in ether. This glyceride is one of the most abundant of the constituents of the natural fats, being found in most liquid fats and oils. Obtained from palm oil or butter, from Chinese vegetable wax by first pressing out and then treating repeatedly with hot alcohol, whereby free palmitic or oleic acids go into solution. The residue is then crystallized out of ether.

Monopalmitin, $C_3H_5(OH)_2OC_{16}H_{31}O$, and *Dipalmitin*, $C_3H_5(OH)(OC_{16}H_{31}O)_2$, have also been prepared artificially from glycerin and palmitic acid.

Tristearin, $C_3H_5(OC_{18}H_{35}O)_3$, occurs in most of the solid fats and in a large number of the liquid fats associated with palmitin and olein. It is difficult to obtain the tristearin perfectly free from tripalmitin, even after repeated crystallizations, but it has been claimed that it can be obtained perfectly free from the seeds of *Brindonia indica*. Fuses at first at 55°, but after repeated melting shows a permanent melting point of 71.5°.

Both *Monostearin*, $C_3H_5(OH)_2(OC_{18}H_{35}O)$, and *Distearin*, $C_3H_5(OH)(OC_{18}H_{35}O)_2$, have been obtained synthetically; the former direct from glycerin and stearic acid, and the latter by the aid of the former.

Triarachin, $C_3H_5(C_{20}H_{39}O)_3$.—This glyceride is found in earth-nut oil as well as in cocoanut oil, and the fat from the seeds of *Nephelium lappaceum*.

Tribenin, $C_3H_5(OC_{22}H_{43}O)_3$.—A glyceride found with olein in oil of ben from *Moringa oleifera*.

Trihypogæin, $C_3H_5(OC_{16}H_{29}O)_3$. —This glyceride occurs along with triarachin and triolein in earth-nut oil.

Triolein, $C_3H_5(OC_{18}H_{33}O)_3$, occurs abundantly in nature in the non-drying fatty oils, as olive and almond oils. May be obtained approximately pure by agitating olive or almond oil with a cold concentrated aqueous solution of caustic soda, which saponifies the palmitin and leaves the most of the olein unchanged. Is liquid at ordinary temperatures, but solidifies below 0°, and can be distilled in a vacuum. Only slightly soluble in alcohol, easily soluble in ether. By treatment with nitrous acid it is converted into solid white elaïdin, a polymeric compound.

Tridoeglin, $C_3H_5(OC_{19}H_{35}O)_3$.—The glyceride of doeglic acid forms the chief constituent of the oil of the doegling, or bottle-nose whale.

Trierucin, $C_3H_5(OC_{22}H_{41}O)_3$.—This glyceride occurs in the oil of the white and the black mustard-seed, in rape oil and grape-seed oil. Nitrous acid converts it into the isomeric *tribrassidin*.

Trilinolein, $C_3H_5(OC_{18}H_{31}O)_3$.—This glyceride is the characteristic constituent of the drying oils, such as linseed oil, poppy-seed oil, sunflower oil, and hempseed oil. It does not yield a solid product with nitrous acid, but is characterized by the readiness with which it absorbs oxygen and thickens with the formation of resinous products.

Triricinolein, $C_3H_5(OC_{18}H_{33}O_2)_3$.—This glyceride is the peculiar constituent of castor oil. It forms a solid polymeric product known as ricinelaidin when treated with nitrous acid.

The vegetable fats seem to be found in all parts of the plant, but especially in the seeds and fruit, although at times in the root and the leaves also ; in the animal, fats are present in all the tissues and organs, and in all fluids except the normal urine. The fats with the carbohydrates and the albuminoids form the three great classes of food materials needed for the animal organism. The great bulk of the natural fats contain four glycerin esters, trilaurin, tripalmitin, tristearin, and triolein. Of these the first three are solid at ordinary temperatures, while the fourth is liquid. The consistency of a fat, therefore, is mainly determined by the proportion of these several ingredients, the solid fats containing larger amounts of palmitin and stearin, and the fatty oils being especially rich in olein.

All the fats are lighter than water ; they cannot be distilled under ordinary pressure without decomposition, acroleïn (see p. 646) being a chief product of the decomposition. While most of them in a pure and fresh condition are colorless and neutral in reaction, by prolonged exposure to the air they undergo change, become yellowish, develop a strong, unpleasant odor and an acid reaction. They become "rancid," that is, the ester decomposes spontaneously, and the free fatty acid is recognizable. Some of the fatty oils, moreover, on exposure to the air absorb oxygen, developing so much heat thereby as to inflame wool and cotton tissues soaked with the oil. Such oils are known as "drying oils." They become thick and finally dry to translucent resinous masses, which makes them of value for painting and varnish-making. These drying oils owe their character mainly to the fact that they are glycerides of linoleic acid (see p. 656) instead of oleic acid.

A classification of the fats, the fatty oils, and the waxes, which is based partly upon physical properties and partly upon chemical differences, is that of A. H. Allen, which is here given :

(*a*) *Olive Oil Group.*—Vegetable oleins. Vegetable non-drying oils. Lighter than groups *b*, *c*, and *d*. Yield solid elaidins with nitrous acid. Includes olive, almond, earth-nut, ben, rape-seed, and mustard oils.

(*b*) *Cotton-seed Oil Group.*—Intermediate between drying and non-drying oils. Undergo more or less drying on exposure. Yield little or no elaidin. Includes cotton-seed, sesame, sunflower, hazel-nut, and beech-nut oil.

(*c*) *Linseed Oil Group.*—Vegetable drying oils. Yield no elaidin. Of less viscosity than the non-drying oils. Includes linseed, hemp-seed, poppy-seed, niger-seed, and walnut oils.

(*d*) *Castor Oil Group.*—Medicinal oils. Very viscous and of high density. Includes castor and croton oils.

(*e*) *Palm Oil Group.*—Solid vegetable fats. Do not contain notable quantities of the lower fatty acids. Includes palm oil, cacao butter, nutmeg butter, and shea butter.

(*f*) *Cocoanut Oil Group.*—Solid vegetable fats, in part wax-like. Several contain notable proportions of the glycerides of lower fatty acids. Includes cocoanut oil, palm-nut oil, laurel oil, Japan wax, and myrtle wax.

(*g*) *Lard Oil Group.*—Animal oleins. Do not dry notably on exposure, and give solid elaidins with nitrous acid. Includes neat's-foot oil, bone oil, lard oil, and tallow oil.

(*h*) *Tallow Group.*—Solid animal fats, predominantly glycerides of palmitic and stearic acids, although butter contains lower glycerides. Includes tallow, lard, bone fat, wool fat, butter fat, oleomargarine, and manufactured stearin.

(*i*) *Whale Oil Group.*—Marine animal oils. Characterized by offensive odor and reddish-brown color when treated with caustic soda. Includes whale, porpoise, seal, menhaden, cod-liver, and shark-liver oils.

(*j*) *Sperm Oil Group.*—Liquid waxes. Are not glycerides, but esters of monatomic alcohols. Yield solid elaidins. Includes sperm oil, bottle-nose or doegling oil, and dolphin oil.

(*k*) *Spermaceti Group.*—Waxes proper. Are compound ethers or esters of higher monatomic alcohols, with higher fatty acids in the free state. Includes spermaceti, beeswax, Chinese wax, and carnauba wax.

The composition of the natural fats as essentially compounds of the fatty acids with glycerin was first definitely ascertained by Chevreul in 1823, and with this knowledge was also indicated the means of decomposing them. Chevreul first used alkalies for that purpose, and that method is still applied if the alkaline salts of the fatty acids (soaps) are desired. For the purpose of obtaining the fatty acids as such, or the glycerin, other methods have been adopted.

We may summarize the several methods employed for this decomposition under three headings, although practically there are additional methods of decomposition in use which involve a combination of several of these general reactions.

1st. The decomposition of the fats by the action of alkalies. This original method of Chevreul is only employed when the manufacture of a soap is the end desired. We may illustrate it

by the example of the reaction between palmitin and an alkali such as would take place in the manufacture of a palm-oil soap.

$$C_3H_5\begin{cases}OC_{16}H_{31}O\\OC_{16}H_{31}O\\OC_{16}H_{31}O\end{cases} + 3HONa = C_3H_5\begin{cases}OH\\OH\\OH\end{cases} + 3C_{16}H_{31}OONa.$$

Tripalmitin. Glycerin. Sodium Palmitate.

2d. The decomposition of the fats by the action of metallic oxides in the presence of water. Chevreul's use of alkalies was replaced already in 1831 by that of lime, suggested by De Milly, and the use of lime and water under pressure constitutes the "autoclave" process of to-day. This will be referred to and illustrated later in a short section on the "Industries of the Fats." Pharmacists make use of a reaction of this kind in the manufacture of lead plaster (**Emplastrum Plumbi,** U. S. P.), in which the olein of olive oil is decomposed by litharge in the presence of water:

$$2C_3H_5\begin{cases}OC_{18}H_{33}O\\OC_{18}H_{33}O\\OC_{18}H_{33}O\end{cases} + 3PbO + 3HOH = 2C_3H_5\begin{cases}OH\\OH\\OH\end{cases} + 3Pb(OC_{18}H_{33}O)_2.$$

Triolein. Glycerin. Lead Oleate.

3d. The decomposition of the fats by the action of steam or water under pressure. The discovery of the possibility of effecting the "saponification" of the fats by water alone, made in 1854 by Tilghman, has since been utilized very extensively under various forms of procedure. The reaction may be illustrated by the decomposition of stearin:

$$C_3H_5\begin{cases}OC_{18}H_{35}O\\OC_{18}H_{35}O\\OC_{18}H_{35}O\end{cases} + 3HOH = C_3H_5\begin{cases}OH\\OH\\OH\end{cases} + 3C_{18}H_{36}O_2.$$

Stearin. Glycerin. Stearic Acid.

The decomposition by sulphuric acid with after-distillation of the fatty acids is nothing more than a saponification by water in the presence of the acid, although with certain classes of fats it has advantages in increasing the yield of solid fat acids.

INDUSTRIES OF THE FATS.

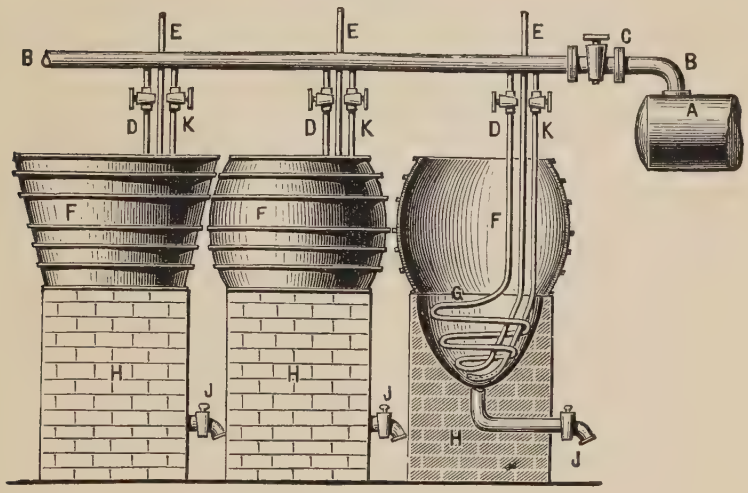
The great importance of many of the vegetable and animal fats as raw materials of large industries justifies us in noticing these industries in outline, and giving a short account of the practical side of them.

1. **Soap-making.**—Soaps are most generally made by the direct saponification of the fat with alkali, although where the fatty acids have been obtained in the free state and then worked, as described later, for the extraction of the solid acids for candle-making, the oleic acid, or "red

oil," remaining over is also utilized for soap-making. Soaps are made chiefly from tallow, cotton-seed oil, cocoanut oil, palm oil, and olive oil. We may divide the soaps, first, into the *hard soaps*, in which the base is soda or a mixture of soda and potash, and *soft soaps*, in which the base is potash. In the manufacture of this latter class the drying oils are preferably used, as in the official **Sapo Mollis**, U. S. P.

True hard soaps are manufactured by boiling the fats in open vessels, with the aid of steam heat, with alkaline lyes of gradually increasing strength, until products of definite character are obtained. The "soap-copper," as shown in Fig. 151, is an iron kettle, or series of kettles, set in

FIG. 151.



Soap-coppers.

masonry and equipped with pipes for both open and closed steam, and provided with an outlet for the discharge of the waste lyes when required. Strong lyes are not used at first or saponification will not take place. A soda-lye of about 11° B., equal to one-fourth that needed for complete saponification, is first run in with the melted fat. When this mixture becomes homogeneous, lye of 20° to 25° B., equal in amount to that taken before, is cautiously added, and boiling is kept up until a sample taken out has a firm consistence between the fingers. It is then salted with a brine of 24° B., and the contents of the copper allowed to stand for several hours at rest. Two layers will then have formed, an upper layer of soap-paste containing water, and a lower one, of "spent-lye," containing the salt and the glycerin in solution. After removing this spent-lye from below, the rest of the caustic soda for saponification is run in and the soap boiled up again.

If a "rosin soap" is desired the rosin is added at this stage, otherwise a "curd soap" is the product. The boiling is now continued until the

frothing subsides and the mixture boils clear. The contents of the copper are then boiled with open steam, and a small quantity of lye of 12° B. is run in until the soap separates in flakes and feels hard when cold. Boiling is usually continued for several hours to insure complete saponification, and it is then allowed to separate and harden. If it is transferred to the cooling-frames before this hardening and separation is completed, a mottled soap may be obtained. A solution of ferrous sulphate added at this point produces a peculiar greenish mottled appearance, becoming red on exposure to the air, characteristic of Marseilles and Castile soaps. In smooth or "cut soaps" water or thin lye is added to the contents of the copper before the soap separates finally to form the curd, and is taken up, giving a smooth yet firm surface to the soap instead of the hard granular appearance of the true curd soap.

In the "cold process" soaps, exact weights of well-refined fats and the necessary caustic soda are used and added together at once. After short standing, they are agitated in a revolving copper provided with paddles at a temperature of not over 120° F. The materials rapidly coalesce, although the reaction is only finished after some days' standing in the cooling-frames. It is obvious that in this case all the glycerin of the fats originally taken remains distributed throughout the soap. Filling and padding materials can also be added in this case, and will be held in the soap. A small quantity of cocoanut oil added to the tallow or other fat facilitates the working of this cold process.

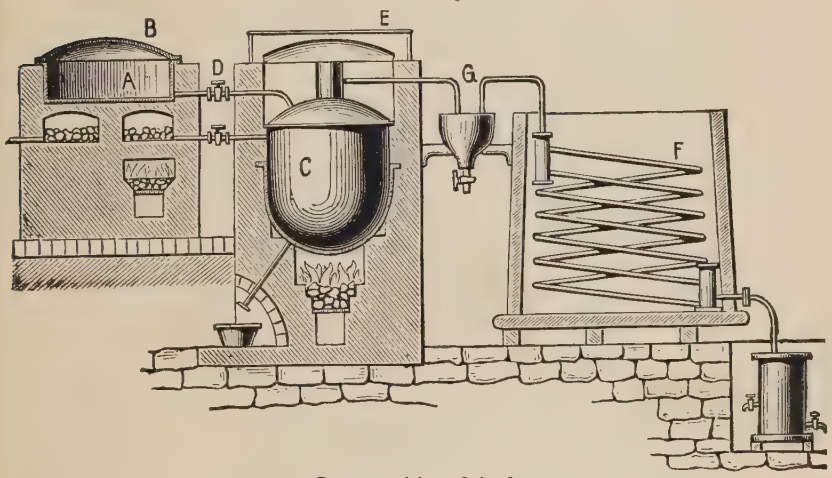
When "red oil" or oleic acid from the stearic acid candle manufacture is used, it may be saponified either with alkali or with alkaline carbonate, although the former is preferred. The oleic acid may also be changed first into the isomeric elaidic acid by the action of nitrous acid, and a very fine soap is then obtained resembling a tallow soap.

Compact soaps may contain from 10 to 25 per cent. of water, smooth or cut soaps may contain from 25 to 45 per cent., and filled soaps from 45 to 72 per cent. of water, besides the glycerin and impurities.

2. **Stearic Acid Candle Manufacture.**—Where the solid fatty acids are desired for the manufacture of candles, the fats are saponified either by the "autoclave process" of Milly, in which lime and hot water, under a pressure of 8 to 10 atmospheres, are made to decompose the fats, or they are decomposed with superheated steam, either with or without the addition of sulphuric acid. In the former process the lime forms a lime soap, which is afterwards decomposed by sulphuric acid, and the free fat acids are thoroughly washed by the aid of steam. The amount of lime taken is not sufficient to completely neutralize the fatty acids, as the steam decomposes the lime soap first formed and allows the base to attack fresh quantities of the fat. In the second process, that of superheated steam, the products are obtained quite pure and free from all foreign matters. As carried out in the Wilson and Gwynne form of apparatus, it is shown in Fig. 152. The fat is first heated in A by waste heat from the superheater below, and then flows into the retort C, which must be kept at from 290° to 315° C., and for this purpose is covered in. The superheated steam at 315° C. comes into the retort by the side tube; after some 24 to 36 hours the contents of the retort are distilled off, the fatty acids con-

densing first, and the watery glycerin passing on to the farther condensing vessel. In this way a very pure commercial glycerin is obtained as well as pure fatty acids. If the temperature much exceed 315° C., acrolein forms from the decomposition of the glycerin. For the extraction of the hard stearic acid the washed fatty acids are now melted and run into troughs or dishes of tin, as shown in Fig. 153. These are placed in a room at a temperature of 20° to 30° C. and kept for two or three days, to allow the palmitic and stearic acids to crystallize, when the contents are emptied into canvas or woollen bags and pressed in an hydraulic press. The liquid oleic acid runs off, and the cakes of crude stearic acid obtained are melted and again put to crystallize at a somewhat higher temperature than before. A thorough pressing will now leave the stearic acid sufficiently firm for candle-making. A little wax or paraffin is usually added to take away the very crystalline structure, which unfits stearic acid somewhat for candle-making.

FIG. 152.



Decomposition of the fats.

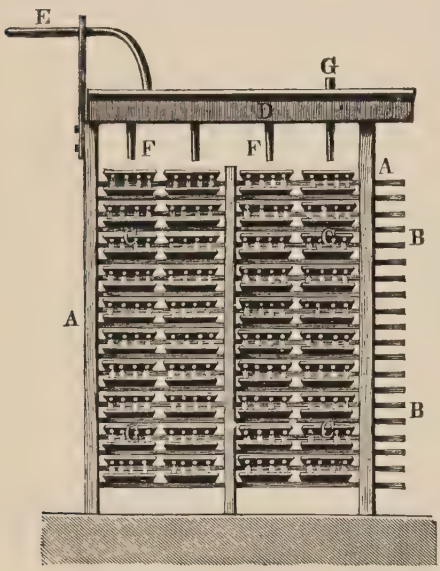
3. Oleomargarine, or Artificial Butter.—When very pure fats are taken and care is exercised in the melting and rendering, it is possible to separate solid stearin by a chilling process similar to that just described for stearic acid, and obtain as a liquid product the mixture of olein and palmitin known popularly as "oleomargarine oil." This so-called "oleo oil" is then churned with about 10 per cent. of its weight of milk, with the addition of a little butter color, and the product is salted and brought into the market as oleomargarine butter. In making what is called "butterine," neutral lard is added to the oleo oil and milk before churning, and then finished as before. At times a small quantity of sesame oil or cotton-seed oil is added to soften the texture of the product.

4. Manufacture of Glycerin and Nitroglycerin.—Glycerin is obtained in connection with the saponification of fats by the autoclave process with

lime or the saponification with superheated steam. The glycerin from the lime process is obtained in a very dilute state at first, and must be concentrated. This is done by the aid of steam, at first with free access of air, and later in vacuo. The product, brought to a specific gravity of 1.22, has a brown color and is known as "raw glycerin." It is then filtered through bone-black in closed and jacketed filters, and distilled with the aid of steam. The glycerin which distils over from the saponification in the apparatus of Wilson and Gwynne, before described, is more concentrated and freer from impurities. It still requires, however, the concentration and after-distillation with steam heat.

Nitroglycerin is a technical product of great commercial importance, because of its large use in mining and blasting operations. It is manufactured on a large scale, but every stage of the process must be watched with the greatest care because of the extreme danger connected with its explosions. The nitrating mixture consists of 5 parts of concentrated sulphuric acid and 3 parts of nitric acid of 1.48 sp. gr. The glycerin must be relatively pure, and of sp. gr. about 1.26. The acid mixture having been placed in a wooden tank lined with lead, and cooled, by coils of leaden pipe through which ice water is circulating, to 14° to 16° C., the glycerin is run in through a small pipe, or, better, in a fine spray through a metal sieve. The liquid must be kept continuously mixed during the nitration, and the temperature not allowed to rise above about 18°. If the temperature rise suddenly or continue rising, the contents of the tank must be allowed to run at once into a larger receptacle containing cold water. The nitration of 730 pounds of glycerin takes from ½ to 2½ hours. When it is completed the product is run into a vessel containing water at 21°. As the nitroglycerin separates, it is then washed first with pure water, then with water containing some soda solution, and finally with strong soda solution. The yield of nitroglycerin is greater in winter than in summer, varying from 950 to 1200 pounds of nitroglycerin from 630 pounds of glycerin. The several operations of nitration, separation, and washing are all carried out in detached buildings, and, as far as possible, compressed air is used for effecting the mixing and washing.

FIG. 153.



Granulation of stearic acid.

5. **The Utilization of the Drying Oils in Paints and Varnishes.**—In the classification of the oils (see p. 674) the distinction was made between drying and non-drying oils. This distinction is based upon differences in chemical composition. The drying oils, like linseed oil, contain large amounts of the glyceride of linoleic acid, which differs from oleic acid chiefly in its power of absorbing oxygen and becoming resinous. This tendency is notably accelerated by boiling the oils with certain mineral compounds like litharge, manganese dioxide, and the acetates and borates of lead, manganese, and zinc. These are known therefore as "dryers" because of the drying quality they impart to the oils. This is of great importance in the manufacture of paints and varnishes. In a paint we have the finely divided color thoroughly rubbed up and incorporated with boiled linseed oil, and this is then thinned out with oil of turpentine. In varnishes we have solutions of hard resins in oil, also thinned out, if necessary, with oil of turpentine. The resins so used are amber, copal, damar, animé, etc.

Printers' ink is also a thoroughly boiled linseed oil varnish with which is incorporated the lamp-black or other color and a small quantity of soap. Oilcloth and linoleum are also products into which boiled linseed oil enters.

VIII. Amines and Amides.

The introduction of an alcohol or basic radical into the ammonia molecule replacing one or more hydrogen atoms gives us an *amine*, and just as ammonia can combine with a haloid acid to form an ammonium salt, so the amine or derived ammonia can unite with the chloride, bromide, or iodide of an alcohol radical to form a derived ammonium salt in which, for instance, the four hydrogen atoms of NH_4Cl may be replaced by alcohol radicals.

We may have *primary*, *secondary*, or *tertiary* amines, according as one, two, or three atoms of hydrogen in NH_3 are replaced. We may also have monamines, diamines, or triamines, according as one, two, or three molecules of ammonia are represented. Thus:

$NH_2.CH_3$, methylamine, is a primary amine.

$NH.(CH_3)_2$, dimethylamine, is a secondary amine.

$N(CH_3)_3$, trimethylamine, is a tertiary amine.

$(NH_2)_2.C_2H_4$, ethylenediamine, is a diamine.

$N(C_2H_5)_4.OH$, tetraethyl ammonium hydrate, is a quaternary base.

$N(CH_3)_4I$, tetramethyl ammonium iodide, is a quaternary salt.

The amines containing the lower alcohol radicals bear a close resemblance to ammonia, being strongly basic, having an ammoniacal odor, forming white clouds with hydrochloric acid, forming salts with haloid acids, which salts unite to form crystalline double

salts with gold and platinic chlorides. The ammonium bases are solid, very hygroscopic, and exceedingly like potash in properties.

The amines are formed by acting directly upon ammonia with the halogen compound of the alcohol radical, only in this case the primary amine first formed again reacts with the haloid compound producing the secondary amine, and so on, so that the result of the reaction is usually a mixture of primary, secondary, tertiary, and even quaternary bases. The nitro-paraffins, like $CH_3.NO_2$, are also reducible with nascent hydrogen to amines. This reaction has less importance here, however, than under the aromatic nitro derivatives like nitro-benzene.

1. **Monamines.**—*Methylamine*, CH_3NH_2, is found naturally occurring in *Mercurialis annua* and *M. perennis*, in herring brine, in the distillation products of wood, bones, and beet-root molasses, and in the products of the decomposition of morphine, codeine, kreatin, sarcosin, and glycocoll. Is most easily prepared from acetamide, caustic soda, and bromine. Colorless gas, smelling like ammonia, and at the same time with a fish-like odor; burns with a yellowish flame. Forms a crystalline hydrochlorate and sulphate.

Dimethylamine, $(CH_3)_2NH$, occurs also in herring brine and is formed in the decomposition of fish. Found also in Peruvian guano and in pyroligneous acid. It results, moreover, from the decomposition of glue and yeast. Liquid boiling at 8°–9° C.

Trimethylamine, $(CH_3)_3N$, is found quite widely distributed, —in the leaves of *Chenopodium vulvaria*, in *Arnica montana*, in *Cratægus oxyacantha*, and abundantly in herring brine. Formed also in the decomposition of lecithin, protagon, neurin, and betaïn (hence in beet sugar molasses distillation), also from alkaloids like narcotine and codeine by the action of alkalies. Liquid, with a strong odor of decomposing fish, boiling at 9° C.

The isomerism of trimethylamine, $(CH_3)_3N$, and propylamine, $C_3H_7NH_2$, has led to the erroneous use of the latter name at times. Thus, the so-called "propylamine hydrochlorate," used at one time in medicine as a remedy for rheumatic ailments, was a salt of trimethylamine.

Tetramethyl Ammonium Iodide, $N(CH_3)_4I$, is obtained readily by the direct action of CH_3I upon ammonia. It crystallizes in white needles or prisms, and has a bitter taste.

Tetramethyl Ammonium Hydrate, $N(CH_3)_4OH$, forms fine hygroscopic needles.

Ethylamine, $C_2H_5.NH_2$, colorless liquid, boiling at 19°, with a

strongly ammoniacal smell and biting taste. It differs from ammonia in dissolving $Al_2(OH)_6$, but does not dissolve $Fe_2(OH)_6$.

Diethylamine, $(C_2H_5)_2NH$, boils at 56°. Does not dissolve $Zn(OH)_2$.

Triethylamine, $(C_2H_5)_3N$, is an oily, strongly alkaline liquid, boiling at 90°. It is found in the decomposition of fish tissue.

Trimethyl-vinyl Ammonium Hydrate (Neurin), $N(CH_3)_3C_2H_3.OH$.—This base, containing the unsaturated radical vinyl, results when lecithin and protagon, which are found in nerve and brain tissue, are boiled with baryta. Very soluble in water, and of alkaline reaction. Extremely poisonous.

Trimethyl-oxyethyl Ammonium Hydrate (Choline or Bilineurin), $N(CH_3)_3(C_2H_4OH).OH$, is found in the bile (χολή, bile), brain, yolk of egg, etc., being combined with glycerin-phosphoric acid as *lecithin*. It is also present in herring brine, hops, beer, and in many fungi. Choline is a strong base, difficultly crystallizable, and deliquescent. It is not poisonous.

2. **Diamines.**—*Ethylene-diamine*, $C_2H_4(NH_2)_2$, is a colorless liquid, boiling at 123°, easily soluble in water, not miscible with benzene and ether. It smells faintly ammoniacal, and has a caustic taste.

Diethylene-diamine, $(C_2H_4)_2(NH)_2$.—This base, known also as "Piperazin," is formed by the heating of the ethylene-diamine hydrochlorate. Rhombic tablets, fusing at 104° and boiling at 145°. Used considerably in medicine because of its solvent action on uric acid and gouty concretions.

Trimethylene-diamine, $C_3H_6(NH_2)_2$.—Oily liquid, boiling at 136°.

Tetramethylene-diamine, $C_4H_8(NH_2)_2$.—This base, known also as "Putrescin," results from the decomposition of flesh, hence contained in the cadaver. The free base smells like spermatic fluid, boils at 156°–157°, and is poisonous. It is also found in the urine and fæces in cystinuria.

Pentamethylene-diamine, $C_5H_{10}(NH_2)_2$.—This base is known as "Cadaverine." It is formed in the decomposition of flesh and fish, and, as the name indicates, is found in the cadaver. The free base boils at 178°–179°, and smells like spermatic fluid. Is poisonous. The chlorhydrate when heated breaks up into piperidine, $C_5H_{11}N$, and ammonium chloride.

The amides and imides are derivatives of ammonia, in which one or more hydrogen atoms are replaced by acid radicals. They are easily distinguished from the amines by their ready saponifi-

cation. They decompose on heating with acids or alkalies, or even with water, into their components, acid and ammonia. They may be formed by the action of ammonia upon the chlorides of the acid radicals, by the dry distillation of the ammonia salts of the fatty acids, and other methods.

Formamide, $HCO.NH_2$, is obtained by heating ammonium formate to 230°. Liquid boiling at 195° with partial decomposition into NH_3 and CO. Its compound with chloral has already been noted (see Chloralamide, p. 645). It dissolves mercuric oxide, forming, with elimination of water, a compound "mercury-formamidate," $\begin{matrix}HCO.NH\\HCO.NH\end{matrix}>Hg$, which is used somewhat in medicine. The compound is stable in the presence of albuminoids, but is decomposed by dilute acids or alkalies, with separation of fine gray metallic mercury.

Acetamide, $C_2H_3O.NH_2$.—Obtained by heating ammonium acetate to 230°. Forms crystals easily soluble in water and alcohol, fusing at 82°, and boiling at 222°. Has a characteristic odor, recalling mice.

Diacetamide, $(C_2H_3O)_2NH$, forms a white mass, fusing at 78° and boiling at 223°.

Triacetamide, $(C_2H_3O)_3N$.—White needles, melting at 79°; neutral reaction.

The amido acids have been noted in part as derivatives under the several fatty acids (see p. 657). Some additional compounds of this class remain to be noted.

Amido-succinic Acid (Aspartic Acid), $COOH.CH_2.CH(NH_2).COOH$, is readily obtained by boiling asparagin with acids or alkalies. Formed also in the decomposition of albuminoids, horn, and glue, with acids or alkalies. It forms small rhombic tablets easily soluble in hot water. Nitrous acid changes it into malic acid.

Amido-succinamide (Asparagine), $COOH.CH_2.CH(NH_2.CONH_2$, occurs very widely distributed in the vegetable kingdom, as in sugar-beets, potatoes, in the shoots of many vegetables, in sweet almonds and asparagus, whence the name. Forms lustrous rhombic crystals, easily soluble in hot water, insoluble in alcohol and ether. Is a monobasic acid, which combines with bases, acids, and salts. It forms a crystalline blue copper salt, which is nearly insoluble in water.

Amido-pyrotartaric Acid (Glutamic Acid), $COOH.C_3H_5(NH_2).COOH$, occurs along with aspartic acid in all the de-

compositions of albuminoids, etc. Forms rhombic crystals, melting at 202°, soluble in water, difficultly soluble in alcohol.

Amido-pyrotartaramide (Glutamine), $COOH.C_3H_5(NH_2).CONH_2$, accompanies asparagin in many plants, and is best obtained from the fresh juice of the sugar-beet.

Appendix to Amines and Amides.—Analogous to the organic ammonia derivatives are the corresponding compounds derived from *phosphine*, PH_3, from *arsine*, AsH_3, and *stibine*, SbH_3. Ethyl phosphine and triethyl-phosphine are both liquids of powerful and disagreeable odor, which readily ignite, and burn in the air like the spontaneously inflammable phosphine. Tetraethyl-phosphonium iodide is also known. The organic arsenic compounds are primary, secondary, and tertiary arsines. Of these the best known are the secondary compounds. When an acetate like $KC_2H_3O_2$ is distilled with arsenous oxide, As_2O_3, there is produced a compound, $\begin{matrix}As(CH_3)_2\\ |\\ As(CH_3)_2\end{matrix}$, known as *cacodyl* (from κακώδης, stinking), together with the oxide of the same, $\begin{matrix}(CH_3)_2As\\ (CH_3)_2As\end{matrix}>O$, known as cacodyl oxide. The crude mixed distillate was first obtained by Cadet, in 1760, and called "alkarsin," and investigated by Bunsen in 1838. The free base cacodyl is of sickening odor, inciting to immediate vomiting.

The antimony, boron, and silicon compounds have also been obtained, the last named derived from SiH_4, resembling the methane derivatives.

Organo-metallic compounds, such as zinc-methyl, $Zn(CH_3)_2$, and zinc-ethyl, $Zn(C_2H_5)_2$; mercury-methyl, $Hg(CH_3)_2$, and mercury-ethyl, $Hg(C_2H_5)_2$; aluminum-methyl, $Al(CH_3)_3$; lead-methyl, $Pb(CH_3)_2$, and lead-ethyl, $Pb(C_2H_5)_2$; and tin-tetramethyl, $Sn(CH_3)_4$, and tin-tetraethyl, $Sn(C_2H_5)_4$, have all been prepared.

IX. Carbohydrates.

We find very widely distributed in the vegetable kingdom a class of compounds which are of the greatest importance as food-products in the support of animal life, and play an important part in the nutrition of the living organism. These compounds have been termed "carbohydrates," because they contain along with carbon the elements hydrogen and oxygen in the ratio of 2 to 1, or as they exist in water. They also bear a simple relation to the hexatomic alcohols mannite and dulcite (see p. 635), the formulas of which were $C_6H_{14}O_6$. As the formula of one group of carbohydrates is $C_6H_{12}O_6$, and several of them can be formed by the careful oxidation of these hexatomic alcohols, it was supposed they were aldehydes or ketones of these alcohols, and such in fact they proved to be. A second group of the carbohydrates, with the formula $C_{12}H_{22}O_{11}$, seem to be simply anhydrides of the

first aldehydic or ketonic group; and the third group, with the formula $(C_6H_{10}O_5)_n$, are still more complex anhydrides. The process of "hydrolysis" is capable of causing these anhydrides to take up water and yield compounds of the other group. Despite the large number of these carbohydrates occurring in nature, until very recently it had not been found possible to form any of them by synthetic means. A beginning has now been made in this work, however, by the German chemist Emil Fischer, and, while the more important of the carbohydrates still remain incapable of artificial formation, the way is clearly indicated. The number of artificial compounds formed makes it necessary to broaden the classification hitherto adopted, and, instead of the old grouping of *Glucoses*, $C_6H_{12}O_6$, *Sucroses*, $C_{12}H_{22}O_{11}$, and *Amyloses*, $(C_6H_{10}O_5)_n$, we now classify them as follows:

1. **Monosaccharides.**—

Trioses.—Glycerose, $C_3H_6O_3$ (prepared from glycerin by oxidation).

Tetroses.—Erythrose, $C_4H_8O_4$ (prepared from erythrite by oxidation).

Pentoses.—Arabinose, $C_5H_{10}O_5$ (prepared by the action of dilute sulphuric acid upon lævo-rotatory gum arabic); xylose, $C_5H_{10}O_5$ (prepared by boiling beech-wood and jute with dilute acids); ribose, $C_5H_{10}O_5$ (prepared from arabinose by heating with pyridine); rhamnose or isodulcite, $C_5H_9(CH_3)O_5$, a methyl-pentose (prepared by the decomposition of glucosides like quercitrin); fucose, $C_5H_9(CH_3)O_5$ (obtained from sea-weeds by hydrolysis).

Hexoses are divided into two groups,—the *aldoses*, in which the aldehydic character is shown, and the *ketoses*, in which the ketone character is indicated by their reactions. To the aldose group belong mannose, $C_6H_{12}O_6$ (obtained by the careful oxidation of mannite); glucose, $C_6H_{12}O_6$ (of which the dextro-rotatory variety is the naturally occurring dextrose); gulose, $C_6H_{12}O_6$ (obtained as yet only artificially); galactose, $C_6H_{12}O_6$ (obtained by the inversion of milk sugar); talose, $C_6H_{12}O_6$ (obtained as yet only artificially); rhamno-hexose, $C_6H_{11}(CH_3)O_6$ (obtained artificially from rhamnose). To the ketose group belong fructose (or levulose), $C_6H_{12}O_6$ (obtained along with glucose in the inversion of cane-sugar); acrose, $C_6H_{12}O_6$ (obtained as yet only artificially); sorbinose, $C_6H_{12}O_6$ (obtained from mountain-ash berries).

Heptoses.—Manno-heptose, $C_7H_{14}O_7$ (obtained artificially from

mannose); gluco-heptose, $C_7H_{14}O_7$ (obtained artificially from glucose).

Octoses.—Manno-octose, $C_8H_{16}O_8$ (obtained artificially from mannose); gluco-octose, $C_8H_{16}O_8$ (prepared from the corresponding glucose).

Nonoses.—Manno-nonose, $C_9H_{18}O_9$ (prepared from the corresponding mannose); gluco-nonose, $C_9H_{18}O_9$ (prepared from the corresponding glucose).

2. Disaccharides and Trisaccharides.—

Tribioses and *Tetrabioses* are as yet unknown.

Pentabioses.—Arabinon, $C_{10}H_{18}O_9$ (has been prepared by the moderated action of dilute sulphuric acid upon arabic acid).

Hexabioses.—Sucrose (cane sugar), $C_{12}H_{22}O_{11}$; lactose (milk sugar), $C_{12}H_{22}O_{11} + H_2O$; maltose, $C_{12}H_{22}O_{11}$; isomaltose, $C_{12}H_{22}O_{11}$; trehalose (mycose), $C_{12}H_{22}O_{11}$; melabiose (eucalyn), $C_{12}H_{22}O_{11}$; turanose, $C_{12}H_{22}O_{11}$ (obtained by the partial hydrolysis of melezitose).

Hexatrioses.—Meletriose (raffinose), $C_{18}H_{32}O_{16}$; melezitose, $C_{18}H_{32}O_{16}$.

3. Polysaccharides.—

(*a*) *Crystallizable Polysaccharides.*—Gentianose (from *Gentiana lutea*); lactosin (from *Silena vulgaris*); and stachyose (from *Stachys tuberifera*).

(*b*) *Uncrystallizable Polysaccharides.*—These include three sub-groups of related compounds:

Starches, lichenin (from Iceland moss), inulin (from *Inula helenium*), triticin, and glycogen (or animal starch).

Dextrine (or artificial gum), natural gums (including gum arabic, wood-gum, bassorin, etc.), and pectin substances.

Cellulose, lignin, and tunicin (or animal cellulose).

The monosaccharides as a class are neutral, taste sweet, and are colorless and odorless. They are all easily soluble in water, difficultly soluble in absolute alcohol, and insoluble in ether. They are easily oxidizable, and therefore all reduce alkaline solutions of metallic salts. The solution usually taken for this reaction is an alkaline solution of copper tartrate known as "Fehling's solution." This reaction takes place quantitatively, and hence Fehling's solution serves as a means of estimating sugars.

The directions of the U. S. Pharmacopœia for its preparation are: "Dissolve 34.64 Gm. of carefully selected, small crystals of pure cupric sulphate, showing no trace of efflorescence or adhering moisture, in a sufficient quantity of water to make the solution measure, at or near

15° C., exactly 500 C.c. Keep this in small, well-stoppered bottles. Dissolve 173 Gm. of potassium and sodium tartrate, and 125 Gm. of potassium hydrate, in a sufficient quantity of water to make the solution measure, at or near 15° C., exactly 500 C.c. Keep the solution in small, rubber-stoppered bottles. For use, mix exactly equal volumes of the two solutions at the time required. One cubic centimeter of the mixed solution is the equivalent of:

	Gramme.
Cupric sulphate, crystallized, $CuSO_4 + 5H_2O$	0.03464
Cupric tartrate, $CuC_4H_4O_6 + 3H_2O$	0.03685
Glucose, anhydrous, $C_6H_{12}O_6$	0.00500"

Very characteristic for the monosaccharides is the reaction with phenyl-hydrazine, $C_6H_5.NH.NH_2$. When this reagent in dilute acetic acid solution is heated with these compounds, these form difficultly soluble and crystalline *osazones*, by means of which they can be separated and identified.

The monosaccharides are not equally subject to the decompositions in the presence of micro-organisms known as "fermentations." The trioses, hexoses, and nonoses appear to be readily fermentable, while the pentoses, heptoses, and octoses are not decomposed.

The trioses, tetroses, and pentoses are not of sufficient importance to require more than the mention already given in the classification. The hexoses, however, include not only a number of important, naturally occurring sugars, but compounds obtained in the hydrolysis of the di-, tri-, and polysaccharides.

Mannose, $C_6H_{12}O_6$, is obtained by the careful oxidation of mannite, and by the hydrolysis by means of dilute sulphuric acid of many natural carbohydrates, such as salep mucilage and hemicellulose from vegetable ivory-nuts, palm-nuts, etc. Hard, friable powder, easily soluble in water, and fermentable with yeast.

Glucose, $C_6H_{12}O_6$.—This is the most widely distributed of the hexose class. It occurs, under the common name of "grape sugar," along with fructose (fruit sugar) in most sweet fruits and juices. Grape juice contains 10 to 30 per cent., figs 12 per cent., sweet cherries 9 to 10 per cent., apples and pears 7 to 10 per cent., plums and apricots 2 to 5 per cent. Small amounts of this sugar are found in the blood as well as in most of the organs and tissues of the body. In the disease known as "diabetes mellitus" the urine contains larger amounts (as high as 8 to 10 per cent.). It is most readily prepared by the hydrolysis (inversion) of the carbohydrates of the higher classes like cane

sugar, which yields a mixture of equal molecules of glucose (dextrose) and fructose (levulose), and starch, which yields products like dextrin and maltose, which gradually pass into glucose. The commercial glucose (or starch sugar) is, however, never perfectly converted, and contains, besides dextrine and maltose, unfermentable sugars as alterative products.

Glucose crystallizes out of alcohol or from concentrated aqueous solution at 30°–35° in anhydrous needles or hard crusts, which fuse at 146°. At ordinary temperatures it crystallizes out of aqueous solution with 1 molecule of water in warty masses. It is distinctly inferior in sweetness of taste to cane sugar.

Galactose, $C_6H_{12}O_6$, is produced along with glucose by the hydrolysis of milk sugar as well as from many other carbohydrates, such as gums. Is also obtained as a decomposition product of the cerebrin of the brain. Crystallizes in small crystals, fusing at 168°, and is fermentable.

Fructose, $C_6H_{12}O_6$, known also as Fruit sugar or Levulose, is found along with glucose, and at times with cane sugar, also in ripe fruits, also found in honey. By boiling cane sugar with dilute acids equal molecules of dextrose and levulose are produced. It is also formed by the decomposition of inulin with dilute acids. Forms a syrup or needles, which unite to rounded aggregates, and fuse at 95°. Tastes sweet, and is lævo-rotatory. Is fermentable by yeast, but more slowly than glucose. It forms a difficultly soluble compound with calcium oxide, $C_6H_9(CaOH)_3O_6$, by means of which it can be separated from the more soluble dextrose compound when the two are present together, as in invert sugar.

Levulose has recently been introduced into medicine under the name of "diabetin," and is made from invert sugar, as indicated above.

Acrose, $C_6H_{12}O_6$ (so named because prepared from acroleïn), is an artificial sugar first made by Emil Fischer, and is interesting as having yielded by various synthetical reactions three other artificial sugars,—mannose, glucose, and fructose.

The heptoses, octoses, and nonoses have as yet only a theoretical interest.

The disaccharides are a most important class, and include several of the best known of the sugars. Under the group hexabioses we have sucrose, or cane sugar, lactose, or milk sugar, and maltose, or malt sugar, as the most important. All these sugars are capable of inversion or hydrolysis in the presence of dilute

acids as well as certain ferments, and then yield products belonging to the class of monosaccharides. Thus, sucrose, on inversion, yields a mixture of dextro-glucose and fructose; milk sugar yields dextro-glucose and galactose; and maltose yields dextro-glucose alone. Milk sugar and cane sugar are not fermentable with yeast until after inversion; maltose is directly fermentable. Cane sugar has no effect upon Fehling's solution, while milk sugar and maltose have a reducing effect.

Sucrose (or Cane Sugar), $C_{12}H_{22}O_{11}$ (**Saccharum**, U. S. P.), is very widely distributed in nature, especially in the sugar-cane (*Saccharum officinarum*), which contains from 16 to 20 per cent.; in the sugar-beet, which contains from 12 to 16 per cent.; in the sorghum-cane, which contains from 7 to 10 per cent.; in the sugar-maple, the juice of which contains from 3 to 4 per cent.; in Indian corn, and in many fruits. The extraction and commercial manufacture is practically limited to the two sources first named, the sugar-cane and the sugar-beet. An outline of the process of manufacture will be appended to this section.

Pure sucrose crystallizes in anhydrous, monoclinic crystals, melting at 160°. Easily soluble in water, difficultly soluble in alcohol, insoluble in ether, chloroform, or carbon disulphide. Is dextro-rotatory, its specific rotatory power being $+66.5°$ for rays $[a]_D$.

The optical analysis of sugar solutions is effected by the aid of the polariscope (see p. 106), an instrument in which the ray of polarized light is made to pass through a definite length (usually 100 or 200 mm.) of a solution made up by dissolving a definite weight of the sugar (26.048 gm. in most instruments) in 100 c.c. of pure water, and filtering if necessary. The plane of the ray is rotated thereby through a certain angle, and on rotating the analyzing prism of the polariscope through a corresponding angle in the opposite direction the effect is just compensated for. The circular scale on the tube rotated is graduated in percentage numbers, so that the percentage strength of the sample in pure sugar can be read off at once.

Cane sugar does not reduce Fehling's solution, nor is it directly fermentable with yeast, as is glucose. Prolonged contact with the yeast, however, brings about an inversion through the action of the soluble ferment *invertin* present in the yeast, and then the products of the inversion, dextrose and levulose, at once ferment. Cane sugar unites with lime and strontia to form insoluble saccharates, such as $C_{12}H_{22}O_{11} + 3CaO$ and $C_{12}H_{22}O_{11} + 2SrO$. Concentrated sulphuric acid dehydrates and chars the sugar, pro-

ducing a coke. Prolonged action of dilute hydrochloric acid converts sugar into levulinic acid (see p. 667).

Lactose, or Milk Sugar, $C_{12}H_{22}O_{11}+H_2O$ (**Saccharum Lactis, U. S. P.**).—This variety of sugar occurs in the milk of the mammalia to the extent of from 3 to 6 per cent., and is usually obtained from the "whey" or thin liquid which remains when the casein has been coagulated by rennet. It crystallizes in hard, white crystals with 1 molecule H_2O. It is less sweet than cane sugar, and less soluble in water; insoluble in alcohol, ether, and chloroform. It is dextro-rotatory, $[a]_D = 52.5°$. It differs from cane sugar in having a direct reducing power on Fehling's solution.

Maltose, $C_{12}H_{22}O_{11}$, results from the action of the diastase of malt upon starch during the germination of cereals (as in malting of grain), and also as an intermediate product on boiling starch with dilute sulphuric acid. It forms fine, white needles, crystallizes with 1 molecule of H_2O, and is easily soluble in water. It is strongly dextro-rotatory, $[a]_D = +137°$. It reduces Fehling's solution, the reducing power being about two-thirds that of glucose, is easily decomposed by alkalies, is fermented with yeast, and yields on hydrolysis with dilute acids only dextro-glucose. Neither maltose nor lactose reduces Barfoed's reagent (an acetic acid solution of copper acetate), and in this way may be distinguished from glucose.

Isomaltose, $C_{12}H_{22}O_{11}$, is formed synthetically from dextro-glucose by the prolonged action of strong hydrochloric acid at 10°–15°, and is contained in commercial starch sugar because of such retrograde action. It is also a product of the action of diastase upon starch, and is present in malt; as it undergoes fermentation only slowly, it is usually present unchanged in fermented malt liquors, such as beer (amounting to 25–30 per cent. of the beer extract at times). It is intensely sweet, and changes at 65° into yellowish-brown products of roasting, which are also sweet and give character to the roasted malt.

The most important trisaccharide or hexotriose is

Melitriose or Raffinose, $C_{18}H_{32}O_{16}$.—This sugar is found in the sugar-beet, and hence obtained in the working of the molasses from the same; also in the Eucalyptus manna, in cotton-seed cake, etc. Is less soluble in water than cane sugar, and almost devoid of sweet taste. Strongly dextro-rotatory, $[a]_D = 103.9°$. It does not reduce Fehling's solution. Readily fermentable with yeast. When inverted, yields first fructose and melibiose

and the latter is then decomposed into galactose and dextro-glucose.

The crystallizable polysaccharides mentioned are as yet of slight importance. The uncrystallizable polysaccharides, on the other hand, include compounds of the greatest importance in the growth of vegetable life, and as the basis of food preparations used for human sustenance.

Starch, $(C_6H_{10}O_5)_n$ (**Amylum**, U. S. P.), is very widely distributed, being contained in all assimilable plants, in which it constitutes a reserve material. As such it is contained especially in the roots, tubers, seeds, fruit, and in the medullary rays of the trees during the winter. During the movement of the sap of the plant it is changed into sugar. Starch is extracted practically from potatoes (containing 21 per cent.), from maize or Indian corn (containing 50 per cent.), from wheat (containing 64 per cent.), and from rice (containing 77 per cent.). Specially rich in starch also are the tropical plants, such as arrow-root, sago, and manihot.

Starch consists of a white, velvety, somewhat hygroscopic powder, recognized under the microscope as made up of granules of round or slightly elongated shape which show a concentric structure. The interior substance of the granule, or the true starch material, is called "granulose," and is readily dissolved under the action of diastatic ferments, while the exterior shell is a cellulose material called "farinose," and is not acted upon by ferments.

The most complete classification of the starches is that of Muter as amplified by Blyth, by which they are divided into five groups, on the basis of their physical and microscopical differences, as follows :

(*a*) *The potato group* includes such oval or ovate starches as give a play of colors when examined by polarized light and a selenite plate, and have the hilum and concentric rings clearly visible. It includes *tout les mois*, or canna arrow-root, potato starch, maranta, or St. Vincent arrow-root, Natal arrow-root, and curcuma arrow-root.

(*b*) *The leguminous starches* comprise such round or oval starches as give little or no color with polarized light, have concentric rings all but invisible, though becoming apparent in many cases on treating the starch with chromic acid, while the hilum is well marked and cracked, or stellate. It includes the starches of the bean, pea, and lentil.

(*c*) *The wheat group* comprises those round or oval starches having both hilum and concentric rings invisible in the majority of granules. It includes the starches of wheat, barley, rye, chestnut, and acorn, and a variety of starches from medicinal plants, such as jalap, rhubarb, senega, etc.

(*d*) *The sago group* comprises those starches of which all the granules are truncated at one end. It includes sago, tapioca, and arum, together with the starch from belladonna, colchicum, scammony, podophyllum, canalla, aconite, cassia, and cinnamon.

(*e*) *The rice group.* In this group all the starches are angular or polygonal in form. It includes the starches of oats, rice, buckwheat, maize, dari, pepper, as well as ipecacuanha.

In addition to the differences in form and marking mentioned above, the starch-granules differ in size according to their different sources, so that under the microscope they can be distinguished by the measurement of the average diameter of the granule. This ranges, according to Karmarsch, from .01 to .185 millimeter, or from .0004 to .0079 inch.

Fig. 154 illustrates some of the most characteristic of these starches as seen under the microscope.

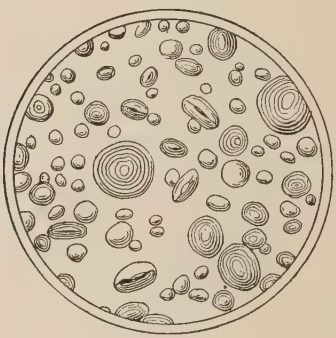
Starch is insoluble in cold water, alcohol, and ether; on warming with water it begins to swell up at 55° C., and at 70° to 80° the granules burst and it becomes a uniform, translucent mass known as "starch paste," which is not, however, a solution, as the water can be frozen out of it. Boiled with water for a long time it goes into solution, one part dissolving in fifty parts of water. The prolonged action of glycerin at 190° also causes the change into *soluble starch.* The action of heat upon starch is to change it gradually into dextrine, which is soluble in cold water. Both the starch-granules and the starch paste are colored intensely blue by iodine. The compound formed is a weak addition compound, and the blue color disappears on heating, but returns again on cooling. This starch reaction serves to indicate the existence of the starch molecule in any vegetable extract, and the gradual breaking down of this molecule under the influence of hydrolysis can also be checked off by noting the iodine reaction. Thus, under the influence of dilute acids dextrin and dextrose are produced, the latter eventually as sole product. Many ferments, like saliva, the pancreatic ferment, and especially the diastase of malt, produce in the starch a somewhat similar change, and yield maltose, $C_{12}H_{22}O_{11}$, and a number of intermediate products between this and starch. These changes

FIG. 154.

Sago.

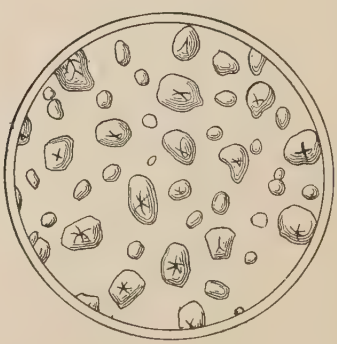
Potato.

Pea.



Wheat.

Rice.



Corn.

and the distinguishing tests by which they may be recognized may be stated as follows:

Starch . . . . . gives a blue iodine reaction.
Soluble starch (amylo-dextrine) . gives a blue iodine reaction.
Dextrines { Erythro-dextrine . . gives a violet and red iodine reaction.
Achroo-dextrine . . gives no iodine reaction.
Malto-dextrine . . . gives no iodine reaction.
Maltose . . . . reduces Fehling's solution but not Barfoed's reagent.
Dextrose . . . reduces Fehling's solution and also Barfoed's reagent.*

Strong nitric acid in the cold acts upon starch, producing nitro derivatives, such as mono-, di-, and tetra-nitro-amylose, collectively known as xyloïdin.

Lichenin is prepared from lichens as a gelatinous mass (Iceland moss), soluble in water, and precipitable in flocks on addition of alcohol.

Inulin $(C_6H_{10}O_5)_2$, is obtained from the roots of *Inula helenium*, from the *Dahlia*, *Helianthus*, and other sources. Forms a white powder made up of microscopical spherules. Easily soluble in water and in copper oxide-ammonia (Schweizer's reagent). Does not reduce Fehling's solution, but does reduce ammoniacal silver solution.

Glycogen, $(C_6H_{10}O_5)_n$.—Known also as animal starch. Is found most abundantly in the livers of mammalia and in notable quantities in the tissues of the embryo. White, amorphous powder, soluble in water to an opalescent dextro-rotatory liquid, which is colored red with iodine. After the death of the animal the glycogen changes to dextrose very rapidly, and the same change takes place when it is boiled with dilute acids, while ferments change it into maltose.

Dextrine, $(C_6H_{10}O_5)_2$.—This substance can be formed from starch by the action of dilute acids, of diastase, or by heat alone. In the latter case the reaction is merely one of molecular rearrangement, and may be approximately expressed by the reaction $2(C_6H_{10}O_5)_3 = 3(C_6H_{10}O_5)_2$. In the other cases it is probable that hydrolysis gives rise to several successive changes, and different dextrines are considered as being formed successively, such as *erythro-dextrine*, *achroo-dextrine*, and *malto-dextrine*. Technically, dextrine is obtained by the heating of starch after moistening with dilute acids. Dextrine is a white or yellowish-brown powder, readily soluble in water, from which solution it may be precipitated on addition of alcohol. Gives a red color with iodine.

* Sadtler's Industrial Organic Chemistry, p. 170.

Is dextro-rotatory. It does not reduce Fehling's solution nor Barfoed's reagent. It is not directly fermentable, but in the presence of diastase it goes over into fermentable products. Dextrine is used as a substitute for the natural gums in calico-printing and manufacture of textile goods for a stiffening material, and for glazing paper and card-board, and enters into many food products.

The natural gums are a class of vegetable products which occur at times as amorphous, translucent, or transparent exudations, as in the case of gum arabic, or are extracted by dilute alkalies from the plants, and then are thrown out of solution on addition of hydrochloric acid and alcohol, as in the case of the wood-gums. These gums are soluble in water, forming thick, sticky solutions, which can be filtered, however. They do not reduce Fehling's solution, but by heating with dilute acids yield monosaccharides like arabinose, xylose, dextrose, and galactose.

Somewhat similar products, but only partially soluble in water, are the vegetable mucilages. These do not dissolve, but swell up with water to form liquids which cannot be filtered.

Gum Arabic (Arabin or Calcium Arabate).—This substance (**Acacia,** U. S. P.) is an exudation from the acacia and mimosa species of Africa and the Orient. It contains about 3 per cent. of ash, and on adding hydrochloric acid to the aqueous solution and precipitating with alcohol, a colorless, amorphous substance is obtained. This is arabic acid. On hydrolysis it yields galactose, arabinose, and a pentabiose named arabinon. The so-called "metapectic acid," from the pulp of the sugar-beet, is considered to be identical with arabic acid.

Related to the acacia gums are *wood-gum*, from the wood of foliage trees, yielding xylose on hydrolysis; *cherry-gum*, the gum of cherry- and almond-trees, yielding *l*-arabinose on hydrolysis; *peach-gum*, from the peach-tree, yielding arabinose and galactose on hydrolysis; *barley-gum*, obtained in the nitrogen-free extractive material of cereals, yielding galactose and xylose.

Bassorin is the mucilaginous constituent of gum bassorin and gum tragacanth (**Tragacantha,** U. S. P.).

Carragheen is the mucilaginous constituent of Irish moss (**Chondrus,** U. S. P.). Is not precipitated from its solutions on addition of alcohol; yields galactose on hydrolysis with dilute sulphuric acid. The pectine substances which are found in certain fruits like apples and pears, and in fleshy roots like the beet and the carrot, are also closely related to the carbohydrates. Their concentrated solutions gelatinize on cooling.

Cellulose is the name given to the material of which the growing plant-cell is composed; as the membrane becomes older incrustations of mineral salts occur, and the cellulose also undergoes partial change into lignin, a closely related substance.

Cellulose is insoluble in the ordinary solvents, and therefore to prepare it in a state of purity the plant-fibres like cotton and flax are treated successively with water, alcohol, ether, dilute alkalies, dilute hydrochloric and hydrofluoric acids. The residual fibre is then chemically pure cellulose. We have an example of this in Swedish filter paper, which has been prepared in this way for quantitative analytical use. The cotton fibre is also conveniently purified, and then furnishes a very pure cellulose (**Gossypium Purificatum, U. S. P.**). Pure cellulose is amorphous, and, as stated, insoluble in ordinary solvents. It is soluble, however, in an ammoniacal solution of cupric hydrate (Schweizer's reagent), and is thrown out of this solution on addition of acids and salts. After washing with alcohol it forms a white, amorphous powder. Boiling with dilute acids converts it into dextrine and dextrose, while concentrated sulphuric acid converts it into *amyloid*, an amorphous, translucent mass.

In the manufacture of parchment-paper advantage is taken of this amyloid formation. Unsized paper is passed rapidly through strong sulphuric acid, which causes a superficial change of the cellulose into amyloid; the paper is then washed with water to free it from the adhering acid and hung up to dry. The paper is thus made much stronger and less pervious to liquids, as the pores are filled with the colloidal cellulose.

A mixture of nitric and sulphuric acids has a "nitrating effect," and gives rise to a series of nitric esters or so-called "nitrocelluloses." Taking the formula of cellulose as $C_{12}H_{20}O_{10}$, we have a series beginning with a dinitrate, $C_{12}H_{18}O_8(NO_3)_2$, and running to the hexanitrate, $C_{12}H_{14}O_4(NO_3)_6$. Of these the highest (the hexanitrate) constitutes the true explosive *gun-cotton*, and is insoluble in alcohol, ether, or a mixture of the two. A mixture of the tetranitrate and the trinitrate, on the other hand, constitutes **Pyroxylin, U. S. P.**, and is soluble in a mixture of alcohol and ether, the solution forming **Collodion, U. S. P.** In the preparation of this latter the Pharmacopœia prescribes the dissolving of 30 gms. of pyroxylin in a litre of the solvent, made up of 3 parts of ether and 1 part of alcohol. From this solution on evaporation of the solvent the proxylin is left as a transparent, flexible film.

Celluloid will be noted under the "Industries of the Carbohydrates," following this section.

Lignin is the alteration substance which in most kinds of wood incrusts the true cellulose. It is not affected by dilute acids and alkalies, but is readily oxidized and dissolved by chlorate of potash and nitric acid. It shows two very characteristic color reactions: it is colored intensely yellow with aniline sulphate, and bright red with a solution of phloroglucin in strong hydrochloric acid. These tests serve to identify bleached wood-fibre in paper in which it may be present.

Tunicin (Animal Cellulose) is a closely related material found in the tissues of some animals (*Ascidia*). It is amorphous, and insoluble in ordinary solvents, but soluble in copper oxide-ammonia solution. It yields glucose on hydrolysis.

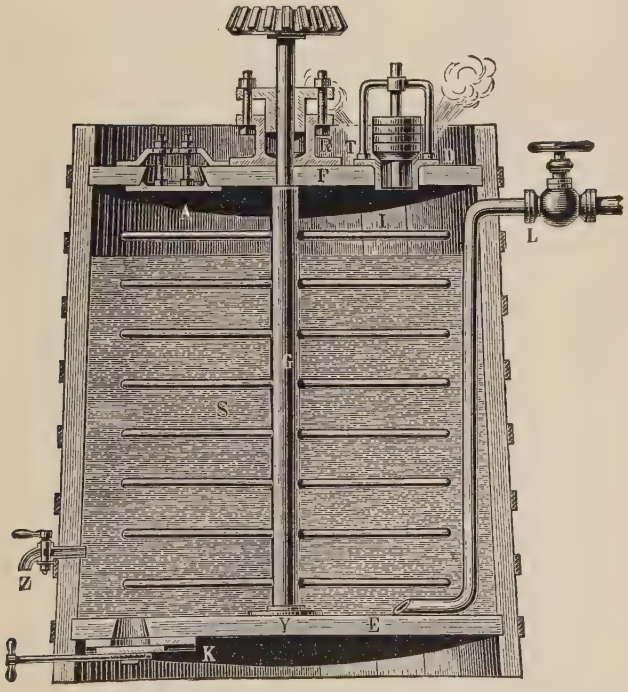
INDUSTRIES OF THE SUGARS, STARCH, AND CELLULOSE.

1. **The Manufacture of Raw and Refined Sugars.**—The two sources for the industrial manufacture of sugars have already been stated to be the sugar-cane and the sugar-beet. The former is grown chiefly in the tropics, West Indies, Java, Brazil, Central America, and Louisiana. The juice is extracted by crushing in roll-mills, or by the process of diffusion, the cane having been cut obliquely in chips. It is at once treated with milk of lime in order to neutralize the organic acids present, which otherwise would start fermentation and rapidly "invert" the cane sugar. This is called "defecating," and causes the rising of a scum of lime-salts, which is skimmed off. The juice properly defecated is then to be evaporated. This is almost universally effected in vacuum-pans, several of which may be connected, forming a "double effect" or "triple effect" pan. By this means the juice is rapidly concentrated at a relatively low temperature, and so the darkening of the product is prevented as well as the formation of molasses. Sulphurous acid or sulphites are also used at times to bleach the juice. The product of this evaporation when allowed to crystallize gives us the raw sugar and a molasses or syrup. This latter is made to yield a second grade of sugar. In the extraction of sugar from the sugar-beet, the process of diffusion is almost universally applied, the beets being sliced and then being placed in large vessels called diffusion-cells. These are arranged in batteries of eight, ten, or a dozen, and warm water is passed through them, taking up successively more and more of the sugar until the solution is quite strong while the beets are becoming more and more exhausted. This solution is then treated with an excess of lime, and the excess removed by what is termed carbonatation with carbon dioxide gas. The insoluble carbonate of lime is then removed by the aid of a filter-press, and the juice obtained clear. The liming and treatment with carbon dioxide may be repeated, and then the juice is concentrated to the crystallizing point in the vacuum-pan. The refining of raw sugars, whether from the sugar-cane or the

sugar-beet, is essentially the same. The raw sugars are "melted," that is, dissolved in hot water, and then the solution is defecated with the aid of blood albumen, filtered through bag-filters (or filter-presses in the case of beet sugar), and then through bone-black, from which it comes practically colorless. It is then evaporated in vacuum-pans to the crystallizing point or "strike," and allowed to cool and thoroughly crystallize. The magma of crystals and syrup is then put into a centrifugal and the syrup separated. The grocery sugars are ready for barrelling as they come from the centrifugal, while the white crystal sugars are dried by a current of hot air before being finished.

2. **The Manufacture of Commercial Glucose.**—This is made exclusively from starch by the action of dilute acids, and in this country the starch used is that obtained from Indian corn. Sulphuric acid is generally employed, and the inversion of the starch is carried out in either open or closed "converters." A form of closed converter early used in the glucose industry is seen in Fig. 155. The amount of oil of vitriol used is

FIG. 155.



Manufacture of glucose.

from one-half pound to one and a quarter pounds per hundred pounds of starch. The starch and water are taken of a gravity of from 18° to 21° B., and the pressure amounts to from forty-five to seventy-five pounds per

square inch. In the manufacture of "glucose syrup," the conversion is not so complete, and the quantity of dextrine is larger than where the solid "grape sugar" is to be obtained as the product. Anhydrous crystallized dextrose can also be obtained as the end product of this inversion of starch by Dr. Behr's patent.

3. **The Manufacture of Starch.**—Starch is obtained commercially from Indian corn, from wheat, and from potatoes. As made from corn in this country, the corn is first steeped in water at a temperature not exceeding 140° F. for from three to ten days, the water being renewed frequently. The softened corn is then ground between burr-stones, while a stream of water is kept running continuously into the hopper. As it is ground, the thin paste is carried on to a series of rotating or shaking sieves. The magma so obtained is then run over inclined sieves of silk bolting-cloth, when the starch goes through as a milky liquid, and is run into settling vats. It is here treated with a weak alkaline solution, to dissolve and remove the gluten, oil, etc., and thoroughly washed by agitation and decantation. It is finally allowed to settle, and dried first in boxes with perforated bottom, and then upon plaster of Paris supports while dried with warm air. 56 lbs. of corn in this way are made to yield 28 lbs. of purified starch. In the manufacture of starch from wheat, the large amount of gluten makes it necessary to take measures to remove it. This is done in the "sour" process by fermentation, the acetic and other organic acids produced rapidly dissolving the gluten and liberating the starch-granules.

4. **The Manufacture of Paper from Cellulose.**—The materials utilized in paper-making are all cellulose-containing substances, such as linen and cotton rags, esparto grass, straw, jute, manila, and wood-fibre. The first chemical treatment after the mechanical preparation of the material is ordinarily the boiling with caustic alkali. In the case of the rags, this has the effect of thorough cleansing; in the case of esparto, straw, etc., it combines with the resin and silica, liberating the cellulosic fibre; in the case of wood, however, the action is necessarily a more fundamental one, as the true cellulose is not only incrusted with mineral matter, but combined with lignin. In the preparation of chemical wood-pulp, however, there are two distinct processes, the "soda-pulp process" and the "sulphite process." In the former, the chipped wood is digested under several atmospheres' pressure with caustic alkali to effect its disintegration; in the latter, calcium or magnesium bisulphite is used, also under considerable pressure, to effect this disintegration. After a thorough washing of the disintegrated pulp, it may be bleached if intended for white paper. This is done with bleaching-powder solution, the excess of chlorine being removed with hyposulphite of soda, known, therefore, as "antichlor." The bleached pulp is then mixed with the proper filling material and sizing, and is ready to go to the "fourdrinier" or paper machine.

5. **The Manufacture of Gun-cotton, Pyroxylin, and Celluloid.**—In the manufacture of the true gun-cotton, the maximum of nitration is sought, and the nitrating mixture is hence of the strongest nitric and sulphuric acids, in the proportion of 3 parts of the latter to 1 part of the former. This acid mixture is cooled first, and then the cotton is immersed and left

for twenty-four hours to complete the nitration. It is then centrifugated, stirred up thoroughly with cold water, again centrifugated and washed systematically with warm water to which some soda has been added. The gun-cotton is usually preserved in the moist state, and dried only when needed for use. The explosive variety of gun-cotton may be used either as loose fibre or as compressed cartridge or paper sheets. When lighted, it burns quickly without smouldering or leaving any residue. When heated slowly it begins to decompose, and above 130° C. it explodes. It is insoluble in water, alcohol, ether, chloroform, and acetic acid, in dilute acids and alkalies. It is somewhat soluble in acetone and wood-spirit.

In the manufacture of pyroxylin, or soluble gun-cotton, the nitric acid taken is less concentrated, and a somewhat higher temperature is used. Potassium or sodium nitrate is also used at times with the sulphuric acid as the nitrating mixture. 20 parts of pulverized potassium nitrate with 31 parts of sulphuric acid of 1.835 sp. gr. may be used. In this mixture the cotton may be left for 24 hours at a temperature of from 28° to 30° C. If relatively stronger nitrating mixtures are used, the time of immersion may be much reduced.

The pyroxylin obtained is washed with cold water until it shows no acid reaction and finally with boiling water.

In recent years an important class of metal varnishes or lacquers have been introduced in which pyroxylin is the basis. This is dissolved in either methyl alcohol, acetone, methyl and amyl acetates, or mixtures of these. Petroleum naphtha is also added to these solvents to facilitate the drying. These varnishes leave a perfectly transparent and flexible film of pyroxylin, which protects the metal to which it has been applied and will not crack or peel when properly used.

The conversion of pyroxylin into celluloid is accomplished by effecting a thorough incorporation with the former of a certain amount of camphor. It is possible to accomplish this by heat alone without the use of any solvent for either the camphor or the pyroxylin, as the camphor at the temperature of its fusion becomes a sufficient solvent for the pyroxylin to effect complete physical admixture. The mixture of the two materials is made while the pyroxylin is still in a partially moist condition, and they are ground together with care in closed drums. The mixture is then put through heated rolls to melt the camphor and cause them to combine. If coloring matter is to be added, it is put in before this melting of the camphor, which distributes it uniformly. The camphor may also be used in solution in methyl or ethyl alcohol.

The product is the well-known celluloid, which may be transparent or opaque, colored uniformly, or mottled and striated in imitation of ivory, coral, amber, tortoise-shell, agate, and other substances. It cannot be caused to explode by heat, friction, or percussion. It is readily soluble in glacial acetic acid, and on diluting with water both camphor and pyroxylin are reprecipitated. It is rapidly soluble in warm, moderately concentrated nitric acid, and also with ease in a hot concentrated solution of caustic soda. Ether dissolves out the camphor from celluloid, and wood spirit behaves similarly. Ether-alcohol (3 to 1) dissolves both the nitro-cellulose and camphor, leaving the coloring and inert matters as a

residue. The density of celluloid ranges from 1.310 to 1.393. When heated to 125° C. it becomes plastic, and can be moulded into any desired shape.

X. Fermentation and Fermentation Industries.

We include under the name of fermentations certain methods of decomposition of organic compounds which presuppose the presence of definite substances called "ferments," which do not, however, apparently take part in the chemical reactions. Their presence in relatively small amount suffices to bring about the decomposition of large quantities of the fermentable material.

The ferments which seem to determine the decomposition may be either soluble unorganized ferments or insoluble organized ferments, which are minute vegetable growths. The decompositions which are brought about by organized ferments differ quite notably in their results from those which can be induced by mere chemical reagents. Thus, the decomposition of sugar into alcohol and carbon dioxide, as it is brought about by the activity of the living yeast-cell, cannot be brought about by purely chemical treatment. On the other hand, the action of the unorganized ferments is much more analogous to that induced by chemical reagents. Thus, the hydrolytic action of diastase on starch can also be perfectly imitated by treating with dilute acids. A distinction is therefore sometimes made between "true distinctive fermentations" and "fermentative decompositions."

With regard to the chemical nature of the *enzymes*, or soluble ferments, we only know that they belong to the class of proteids. A recent analysis of diastase by Lintner may be taken as typical of the class: carbon, 46.66 per cent.; hydrogen, 7.35 per cent.; nitrogen, 10.42 per cent.; sulphur, 1.12 per cent.; and oxygen, 34.45 per cent.

While soluble in water and glycerin they are insoluble in alcohol, and are precipitated from aqueous solution on addition of lead acetate. Their activity is destroyed by heating, that of diastase at 75° C., and all by boiling with water. Their activity is not destroyed by the presence of antiseptics, which arrest the action of the organized ferments. Thus, chloroform, thymol, and salicylic acid will all arrest the activity of the organized growth but not interfere with that of the soluble ferments. Sodium fluoride in 1-per-cent. solution is said to entirely check the growth of the organized ferment, but is without action on those which are soluble.

Foremost among the soluble ferments is *diastase*. This is the ferment formed from the albuminoids of the cereals during the process of germination. It is specially developed in the malting process as applied to barley. Its chief function is the saccharification of the starch of the grain, changing it into dextrine, maltose, and dextrose. The chemical reactions may be summarized as follows:

$$(C_6H_{10}O_5)_3 + H_2O = C_{12}H_{20}O_{10} + C_6H_{12}O_6.$$
$$(C_6H_{10}O_5)_3 + 2H_2O = C_{12}H_{22}O_{11} + C_6H_{12}O_6.$$
$$(C_6H_{10}O_5)_3 + 3H_2O = 3C_6H_{12}O_6.$$

The amount of starch that a given quantity of diastase can convert cannot be stated with absolute certainty, as it varies with the conditions of its preparation, the strength of the infusion, and other points. Its progress can, of course, be controlled by the iodine reaction, as stated under starch. Commercial extracts of malt are infusions of malted barley, which contain the products of the inversion of the starch. The solid extracts obtained by evaporation of these infusions in vacuo at low temperatures should be readily soluble, and should show that they still contain active diastatic ferment by being able to convert their own weight of starch within a short time. The saliva also contains a soluble ferment, which is sometimes called salivary diastase, because of its similarity to the vegetable diastase. The name *Ptyalin* is also given to this substance at times. Another ferment of similar character is the *amlyopsin* of the pancreatic juice.

Invertin (or Invertase) is found in the yeast-plant, and is capable of inverting cane sugar according to the reaction $C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$. Its presence here explains why cane sugar will ferment in the presence of yeast after some considerable time, the invertase having meanwhile caused its change into invert sugar. The same ferment seems to be present in the intestinal juice where its function is to make the cane sugar of foods assimilable by first converting it into invert sugar.

Emulsin (or Synaptase) is found in sweet and bitter almonds. Its function as a soluble ferment is to decompose glucosides. Thus, it decomposes the amygdalin of the bitter almond, salicin, helicin, phloridzin, and arbutin.

Myrosin is a similar ferment found in the black mustard seeds, which by its action on the myronate of potash in the seed liberates the mustard oil as one of the decomposition products.

Pepsin, contained in the gastric juice of animals, and *trypsin*,

found in the pancreatic juice, both have what is termed a "proteolytic" power, or ability to digest or decompose proteid matter.

Pepsin, U. S. P., is described as "a proteolytic ferment or enzyme obtained from the glandular layer of fresh stomachs from healthy pigs, and capable of digesting not less than 3000 times its own weight of freshly coagulated and disintegrated egg albumen." It is obtained as a fine white or yellowish-white powder or in scales or grains, soluble in water or glycerin, but insoluble in alcohol. It can bear a dry heat of 110° without losing its activity, but heated with acidulated water to 100° it is deprived of all proteolytic power. The products which result from the action of pepsin and trypsin upon albuminoid material are called *peptones*. The pancreatic juice contains besides the trypsin another soluble ferment known as *steapsin*, which has the power of emulsifying and partially saponifying fats. The mixture of enzymes naturally existing in the pancreas of warm-blooded animals and usually obtained from the fresh pancreas of the hog is the **Pancreatinum**, U. S. P.

Corresponding to these peptonizing ferments of animal origin is a vegetable ferment, *papaïn*, obtained from the milky juice of *Carica papaya*. It is a white, amorphous powder, soluble in water and glycerin. It peptonizes proteids very readily, acting like trypsin. It is claimed for it, moreover, that it digests and removes the membrane of croup and diphtheria.

The ferment which is extracted from the mucous membrane of the stomach, and which has the power of coagulating the casein of milk, has been called *rennin* (or présure). The preparation called rennet is usually obtained from the stomach of the calf.

Urease is the name given to the enzyme which, equally with organized ferments, is capable of bringing about the ammoniacal fermentation. The reaction for the decomposition of urea is $CO(NH_2)_2 + 2H_2O = (NH_4)_2CO_3$.

A few additional enzymes have been specifically studied, such as *pectase*, characteristic of the pectic fermentation of fruits, etc.

The organized ferments or vegetable growths may be divided into three classes: first, mould growths; second, yeast-plants, or the different species and varieties of *Saccharomyces;* and third, bacteria, belonging to several different genera.

The mould growths at times are able to induce fermentations, but their action consists much more in secondary changes effected in the fermenting bodies or the products of fermentation. *Penicillium glaucum*, the most widely distributed mould growth, is

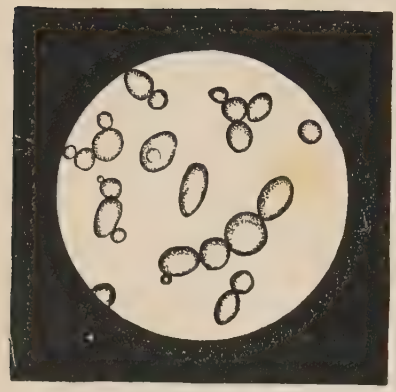
capable of bringing about a number of chemical decompositions. It is said to furnish a soluble ferment capable of inverting cane sugar. *Aspergillus glaucus* possesses a diastatic ferment. For the preparation of the Japanese saké (or rice-wine) is used the *Aspergillus oryzæ*, which comes on the rice grains. The varieties of Mucor (*M. racemosus* and *M. mucedo*) develop some degree of fermentation in dextrose, invert sugar, and maltose. *Oidium lactis* is found in milk.

Much the best defined of all these changes, however, is the alcoholic fermentation as developed by the activity of the yeast-plant. As before stated, it is sugars of the formula $C_6H_{12}O_6$ that are directly acted upon. According to Pasteur, about 95 per cent. of the sugar is decomposed, according to the reaction $C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$, while the rest is decomposed according to secondary reactions, yielding a variety of products, of which glycerin and succinic acid are the most notable. This most important reaction is developed by the species of the genus *Saccharomyces*. The species *Saccharomyces cerevisiæ* is recognized as the special ferment of beer, while *Saccharomyces ellipsoideus* is the ferment of wine. Of the *S. cerevisiæ*, moreover, two well-characterized varieties can be distinguished. The first of these is most active at ordinary temperatures (16°–20° C.), and develops its full fermentative activity in the course of 3 to 4 days; the second develops its activity at a lower temperature (6°–8° C.), and the action is much slower. The first of these yeast-plants, placed in a sugary liquid, is brought by the liberated carbon dioxide to the surface, and hence is said to develop a surface fermentation, while the second remains at the bottom during its whole activity, and the action is called a bottom fermentation. Upon the use of these two varieties are based two quite distinct methods of beer brewing.

Within recent years much attention has been paid to pure cultures of the yeast-plant, and in this way much more regular and uniform fermentations have been produced with the result in a better product. This work has been done largely by Hansen, of Copenhagen, and the microscopical appearance of three of these pure cultures and the ascospore formation of the same are shown in Fig. 156. Of these illustrations, the *Saccharomyces cerevisiæ* and *S. pastorianus* are beer ferments, while *S. ellipsoideus* is the wine ferment.

The special conditions of the alcoholic fermentation are: first, an aqueous sugar solution containing 1 part of sugar to from 4

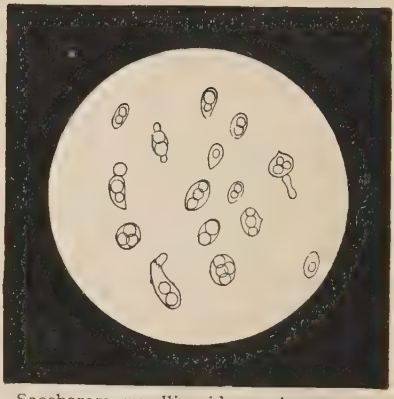
FIG. 156.



Saccharomyces cerevisiæ.

Saccharomyces cerevisiæ. Ascospores.

Saccharomyces ellipsoideus.



Saccharomyces ellipsoideus. Ascospores.

Saccharomyces pastorianus.

Saccharomyces pastorianus. Ascospores.

to 10 parts of water. Second, the presence of a yeast ferment. If this is not added in already developed and active condition, or if the fermentation is to be a spontaneous one,—that is, brought about by the spores present in the air,—the conditions for the growth of the yeast-spores must be present; the solution must contain protein material and phosphates of the alkalies and alkaline earths. Third, the temperature must range between the limits 5°–30° C., or, more narrowly, 9°–25°. Above 30° the butyric fermentation tends to develop rather than the alcoholic, and other decompositions ensue.

The number of changes brought about by organized ferments of the third class or bacteria is very great. Thus, *Bacillus subtilis*, *B. amylobacter*, and *B. termo* bring about a peptonization of albuminoids which, under the influence of these bacteria, decompose into leucin, tyrosin, and ammonia. The butyric acid ferment seems to be the starch-converting *Bacillus amylobacter* (*Clostridium butyricum*, *Vibrio butyricus*), although butyric acid is not the only product developed by it. Under the influence of this bacterium, along with butyric acid, starch solutions yield dextrine and sugar. *Bacterium termo* develops, also, a general putrefaction. As lactic acid ferments, a number of bacteria, which have been only partially studied, are designated. The ones most widely distributed are *Bacillus acidi lacti* and *Micrococcus prodigiosus*.

The acetic fermentation is developed by at least three kinds of bacteria. *Bacterium aceti* was discovered by Pasteur, while Hansen has found two additional acetic ferments, *Mycoderma cerevisiæ* and *Mycoderma pasteurianum*, the latter being the most characteristic.

A series of bacteria which develop turbidity in beer as well as an unpleasant odor and taste are known collectively as "Sarcina." The most important of them, discovered by Lintner, is *Podiococcus cerevisiæ*.

The acetic fermentation is that which most readily develops from the alcoholic and follows it often as a spontaneous change. It requires, besides the presence of a dilute alcohol or alcohol containing liquid, the presence of nitrogenous compounds and salts, and is, above all, what is termed an *aërobic* fermentation,—that is, requires the presence of oxygen. The temperature most favorable for the development of the acetic ferment is between 18° and 35° C. The reaction is purely one of oxidation, $C_2H_6O + O_2 = C_2H_4O_2 + H_2O$, and can be brought about by

chemical means, such as the action of platinum black on dilute alcohol, etc.

The lactic fermentation takes place without the necessity of oxygen, and hence is termed an *anaërobic* fermentation. It takes place in neutral or alkaline solutions, and is hindered by the presence of small amounts of acid. By it galactose, from the inversion of sugar of milk, is simply decomposed, according to the reaction $C_6H_{12}O_6 = 2C_3H_6O_3$. The most favorable temperature is from 35° to 40° C.

The butyric fermentation is like the lactic, and generally fol-

FIG. 157.

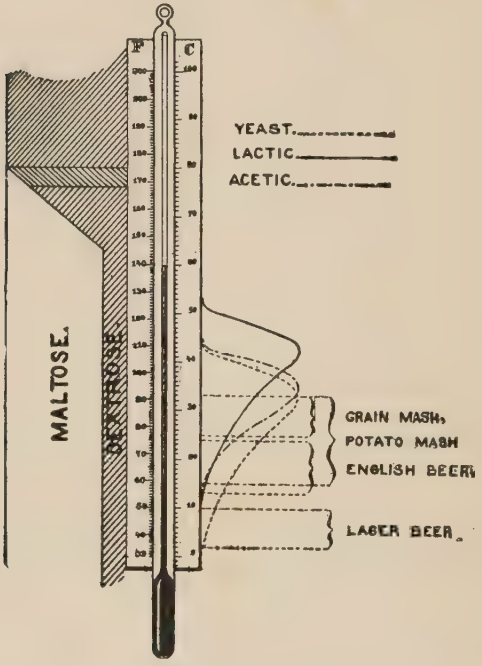


Diagram of temperatures.

lows it. It is also *anaërobic*. The reaction for the production of butyric acid by this fermentation is $2C_3H_6O_3 = C_4H_8O_2 + 2CO_2 + 2H_2$. Other organic compounds, besides sugar, are capable of undergoing this fermentation. Glycerin, under the influence of bacteria, is decomposed into normal butyl alcohol, normal butyric acid, ethyl alcohol, and caproic acid. As the conditions for the lactic and butyric fermentations, both as to

temperature and absence of free oxygen, exist in the intestines, these fermentations take place there, the sugars, organic acids, soluble proteids, and mucus being the material acted upon. The products, as seen in the reactions above, are lactic and butyric acids and carbon dioxide and hydrogen gases. These gases distending the bowel produce the painful symptoms of colic, etc.

The effect of temperature upon the several ferments is shown in the graphic illustration Fig. 157, as well as the influence of temperature upon the decomposition of starch by diastase. On the right side of the figure the regularly-dotted line represents the yeast curve. As the temperature rises from 0° C. its activity increases until the maximum is reached at about 33° C., when it diminishes again, and at 50° or thereabouts it is killed. The activity of the acetic ferment is represented at the same time by the irregularly-dotted line, and that of the lactic ferment by the black line.

FERMENTATION INDUSTRIES.

The most important industrial utilizations of the results of fermentation are those in which the alcoholic fermentation of sugar- and starch-containing materials enters.

1. **The Malting and Brewing of Beer, Ale, etc.**—Malt liquors, as they are termed, are the products of the fermentation of infusions of malted grain, flavored by the bitter extract from hops, and contain from 3 to 7 per cent. of alcohol, together with extractive matter made up of the peptones from the alteration of albuminoids and the carbohydrates from the alteration of the starch of the original grain. The malting process is carried out so as to allow the barley or other grain to germinate, whereby the character of the albuminoids is changed and the ferment diastase is developed, which then begins to act on the starch, the germination and change being stopped at a certain stage by heating in a kiln. Besides the diastase, a second soluble ferment is formed during the malting process, the so-called "peptase," which in the mash process changes the proteids of the malt into peptones and para-peptones, which give nutritive value to beer. Wheat, corn, and rice are used at times as partial substitutes, but the bulk of the grain used is always barley. The finished malt is always yellow or amber-colored shading to brown. The crushed malt is then put through what is termed the mashing process, which is for the purpose of obtaining an infusion containing maltose and dextrine, as well as to allow the diastase to complete the hydrolysis of the starch, changing it into the products before described under the Carbohydrates. This infusion is then strained off and boiled while the hops are added. The "wort," as the liquid is now called, is then cooled, preparatory to the fermentation. This cooling is effected as rapidly as possible, so that the lactic fermentation and similar changes may not develop, and that the spores of foreign yeast ferments may not have access to the

liquid. The thick magma of yeast-cells is then added in the proper amount and the fermentation started, which, as before stated, may be a surface fermentation or a bottom fermentation, according to the temperature and the character of the yeast used. The products differ according to the character of the malt used, whether light or dark, and the character of the fermentation, whether a rapid or a slow one.

2. **The Manufacture of Wines.**—While the name wine is often used to include products of the spontaneous alcoholic fermentation of any sweet fruit or berry, it is usually limited to the product of the fermentation of the grape, which alone is cultivated on an extensive scale throughout the civilized world for the manufacture of wine. The raw material here is the "must," or expressed juice of the grape, which may be fermented either alone or in contact with the "marc," as the pressed pulp and skins are called. The must contains: first, from 16 to 28 per cent. of fermentable sugar (a mixture of dextrose and levulose); non-nitrogenous extract (pectin substance and salts, chiefly of tartaric acid); albuminoids, and free acids (tartaric, malic, and succinic). The percentages of the sugar and the free acids are the most important elements in deciding the probable value of the wine obtainable from the must. The fermentation is a spontaneous one and a protracted one, as, after the full development of the alcoholic strength of the wine, it is left to ripen and develop by an after-fermentation the fruit essences or esters, which give the flavor and bouquet to the wine. In the case of red wines, the main fermentation is allowed to take place with the marc added to the must, so that as the alcohol is developed it may dissolve out the coloring matter of the skins as well as some of the tannin, which is of benefit in effecting a more rapid separation of the protein materials. During the secondary fermentation these deposit upon the inner walls of the storage casks *argols*, or impure acid potassium tartrate (German, weinstein), with some yeast and albuminoid matter. The first fermentation of the must lasts from 1 to 4 weeks, the secondary fermentation from 3 to 6 months, and then the wine is put into casks to ripen, which continues during from 2 to 8 years.

In the manufacture of champagnes and effervescing wines, after the secondary fermentation is nearly finished a mixture of alcohol and pure cane sugar is added, and the wine is bottled so that the supplementary fermentation may continue and develop alcohol and carbon dioxide again. The pressure which develops from this dissolved gas may rise to from 4 to 5 atmospheres.

The percentage of alcohol by weight in wines varies within wide limits, ranging from 5 per cent. in light Rhine wines to 18 per cent. in sherry and port wine.

3. **The Manufacture of Distilled Liquors or Ardent Spirits.**—In this industry the effort is made to push the fermentation to the fullest possible limit, so that the maximum quantity of alcohol may be produced, and then this product of fermentation is distilled, and it may be redistilled in order to get a distillate richer in alcohol than the fermentation product itself can be. The end product sought may be either an alcoholic beverage, which is the product of the distillation, or a raw spirit, which is then redistilled and strengthened until the "rectified spirit" is obtained, which

is used as the basis of many lines of manufacture for the chemist and the pharmacist. The raw materials for this industry may be: first, alcoholic liquids themselves, products of fermentation, which are to be redistilled (such as wines used for manufacture of brandies); second, sugar-containing materials (such as cane-molasses used for manufacture of rum, and beet-molasses and sweet fruits used for fruit brandies); and third, starch-containing cereals and all materials capable of hydrolysis by diastase and fermentation (such as corn, rye, barley, rice, and potatoes). In case the last-named materials are used, the preparation of the wort is the first step. This is analogous to the method already described under malt liquors, except that the whole of the starch is to be converted if possible into maltose, which is directly fermentable, and the dextrine must be thoroughly changed into sugar. The fermentation of the distiller's wort is also somewhat different from that of the brewer, as the maximum percentage of alcohol is to be attained. The yeast is, therefore, a surface yeast, and a maximum temperature of 33° to 34° is attained.

In case molasses is to be fermented for rum, the fermentation is a spontaneous one, the nitrogenous matters present making the addition of yeast unnecessary.

The product of the first distillation of any of these thoroughly fermented mixtures, especially those obtained from grain mashes, is a "raw spirit," containing sharp, aldehydic constituents on the one hand, and higher alcohols (fusel oil) on the other hand, in addition to the ethyl alcohol. These are, as far as possible, to be eliminated or changed by the process of rectifying, and then by storage the supplementary changes of the higher alcohols into ethers are completed.

Rectified Spirit is the most concentrated alcohol obtainable by distillation. The U. S. Pharmacopœia, under **Alcohol**, U. S. P., calls for a spirit containing 91 per cent. by weight of real alcohol, and of sp. gr. 0.820.

Proof-Spirit has a sp. gr. of 0.9198 at 15.5° C., and according to Fownes contains 49.24 per cent. by weight of alcohol.

Brandy (**Spiritus Vini Gallici**, U. S. P.) is, or should be, the direct product of the distillation of French wines. A great deal of it, however, is factitious, being mixtures of grain-spirit and water to which different coloring and aromatic substances have been added.

Whiskey (**Spiritus Frumenti**, U. S. P.) is the spirit obtained from the fermented wort of corn, rye, and barley, either raw or malted.

Rum is a spirit obtained in the West Indies from the molasses of the sugar-cane by fermentation and distillation.

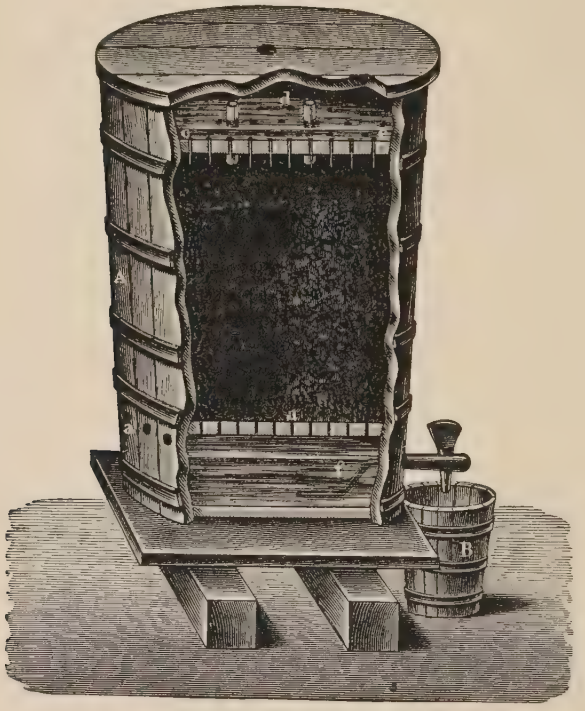
Gin is common grain-spirit distilled and aromatized with juniper berries.

4. The Manufacture of Acetic Acid and Vinegars.—The acetic ferment, as before stated, requires for its growth the presence of oxygen. When the germs coming from the air drop into a fermenting or sugary liquid which is suited for their growth they develop rapidly over the surface of the liquid and form a gelatinous skin, which thickens and falls to the bottom of the vessel because of its increasing weight. Another skin forms at once again, and this in turn is replaced by a third, and so on until the liquid is exhausted of assimilable material. This skin, called

the "mother of vinegar," consists of a multitude of minute fissure ferments. The raw materials furnishing vinegar under the influence of the acetic fermentation are, first, wine; second, spirits; third, malt wort or beer; fourth, fermented fruit juices other than wine; and fifth, sugar-beets. The wines used are those of inferior vintages and such as are unfit for drinking as wine. They should not exceed 10 per cent. in alcoholic strength. The spirits used for vinegar-making must be so diluted with water and vinegar already formed that the alcoholic strength ranges between 3 and 10 per cent. The malt wort used for malt vinegar is completely fermented and then passed through a filter of wood chips into the acetifier. Cider from apples and perry from pears are about the only fruit juices besides wine fermented for the production of vinegar. Sugar-beets are used somewhat in France for vinegar-making.

Three vinegar-making processes are in use with some special modifications. First, the Orleans process, in which a series of mother-casks or

FIG. 158.



Quick-vinegar process.

"acetifiers" holding from fifty to one hundred gallons are used. These are partially filled with hot vinegar, and the wine is added in successive portions, and corresponding portions siphoned off into storage-vats at intervals. The wine vinegars obtained in this way have an agreeable aroma,

that made from white wines being the most esteemed. The second process is the so-called "quick-vinegar process." It is used in Germany and this country for spirit vinegar, and in England for malt vinegar. The vinegar-former is shown in Fig. 158. About a foot above the true bottom of the cask it has a false bottom perforated, as shown in the illustration. The space between the false bottom and a wooden disk set in near the top is filled with beech-wood shavings. Just under the false bottom a series of holes is bored in the side of the cask extending all the way around. The shavings are first boiled in water and dried, then soured or soaked in warm vinegar for twenty-four hours before being put in the cask. Air circulates through the space filled with the beech shavings, entering through the holes below, and escaping through the glass tubes in the wooden disk above. The weak alcoholic liquid is then allowed to slowly trickle down through the shavings. The third process is Pasteur's process, using the vinegar fungus, or "mother of vinegar" directly, and causing it to propagate in a liquid containing suitable food (phosphates of potassium, magnesium, and lime).

Cider vinegar, as is well known, is the result of a spontaneous acetification. The different vinegars may contain from 3½ to 6 or even 8 per per cent. of acetic acid. The other constituents vary with the different kinds of materials used in the vinegar formation.

Factitious vinegars are often made from pyroligneous acid flavored with acetic ether and colored with caramel color.

XI. Derivatives of Carbonic Acid.

Carbonic acid, $CO(OH)_2$, is not known in the free state, but is supposed to exist in aqueous solution in water charged with CO_2. Both this anhydride and the metallic salts of carbonic acid have already been discussed under Inorganic Chemistry, but a number of organic compounds may properly be considered as derivatives of it, and will be mentioned.

1. Sulphur Derivatives of Carbonic Acid.—From the anhydride carbon dioxide we have, by replacement with sulphur, two derivatives:

Carbon Oxysulphide, COS, is formed when a mixture of sulphur vapor and carbon monoxide is led through a red-hot tube, $CO + S = COS$; also by heating together urea and carbon disulphide, according to the reaction: $CO(NH_2)_2 + CS_2 = COS + NH_4CNS$.

Very inflammable gas, of peculiar odor, burning with blue flame.

Carbon Disulphide, CS_2 (**Carbonei Disulphidum**, U. S. P.), is formed by heating carbon in sulphur vapor. When pure, has but slight odor, and is a colorless, highly refractive liquid. After exposure to the light it takes a yellow color from liberation of

sulphur, and develops an offensive odor. Boils at 47°, solidifies at —116°, and melts again at —110°. Easily soluble in alcohol, ether, chloroform, benzene, fixed and volatile oils; insoluble in water. Sp. gr. 1.268. Inflammable, burning with bluish flame. Is used for dissolving caoutchouc and for the extraction of fats and fatty oils from oil seeds and from bones and wool.

Three thio-carbonic acids are possible, $CS\begin{cases}SH\\SH\end{cases}$, $CO\begin{cases}SH\\SH\end{cases}$, and $CS\begin{cases}SH\\OH\end{cases}$. Of these, it is only necessary to consider the last, derivatives of which possess some importance. The ethyl derivative of this acid is called

Xanthogenic Acid, $CS\begin{cases}SH\\OC_2H_5\end{cases}$.—The potassium salt of this acid is formed when carbon disulphide is added to alcoholic potash solution. This salt, $CS\begin{cases}SK\\OC_2H_5\end{cases}$, is used extensively as an antidote for the *phylloxera* insect in the diseases of grape-vines and in the manufacture of artificial indigo. The copper salt, known also as "cuprous xanthate," is a yellow, insoluble compound, the formation of which serves as a characteristic test for carbon disulphide.

2. Esters of Carbonic Acid.—Both the neutral ester, $CO(OC_2H_5)_2$, known as ethyl carbonate, and the acid ester, $CO\begin{cases}OH\\OC_2H_5\end{cases}$, known as ethyl-carbonic acid, are known. The former is a neutral liquid of agreeable odor, lighter than water, and insoluble in the latter. Boils at 126°. The latter is the counterpart of ethyl-sulphuric (sulphovinic) acid, and is not known in the free state, but only in its salts.

3. Chlorides of Carbonic Acid.—From the anhydride carbon dioxide we have the derivative *carbon oxychloride*, $COCl_2$. It is obtained by the direct combination of carbon monoxide and chlorine in sunlight, and also by the oxidation of chloroform by means of chromic acid. It is a colorless gas (known also as phosgene gas), condensing to a liquid below 8°, and of powerful, suffocating odor. It is employed in the preparation of salicylic acid from benzene.

Chloro-carbonic Acid, $COCl(OH)$, is the acid chloride of carbonic acid. Both the free acid and the metallic salts are unstable, and cannot be obtained. Its esters, however, can be prepared, as $COCl(OC_2H_5)$, which is obtained by the action of phosgene gas upon absolute alcohol.

4. Amides of Carbonic Acid.—From carbonic acid we may obtain two amides, both compounds of importance, $CO\begin{cases} OH \\ NH_2 \end{cases}$, known as carbamic acid, and $CO\begin{cases} NH_2 \\ NH_2 \end{cases}$, carbamide or urea.

Carbamic Acid, $CO(NH_2)OH$, is not known in the free state. The alkaline and alkaline earth-salts, however, are well known. The ammonium salt is recognized as present in the official **Ammonii Carbonas, U. S. P.** It results whenever dry carbon dioxide and ammonia gases are allowed to react on each other: $CO_2 + 2NH_3 = CO\begin{cases} ONH_4 \\ NH_2 \end{cases}$. When heated it loses a molecule of water, and urea is formed. The esters of carbamic acid are called *Urethanes*.

Ethyl-urethane, $CO\begin{cases} OC_2H_5 \\ NH_2 \end{cases}$.—This is the compound usually known under the simple name of "Urethane." It is formed by the action of an excess of alcohol upon urea nitrate in closed vessels at a temperature of 120°–130°, the products of the reaction being ammonium nitrate and ethyl urethane. It forms colorless, prismatic crystals, fusing at 47°–50°, which are almost odorless, and have a saltpetre-like taste. Soluble in water. Is used as a soporific.

Chloral-urethane (or Uraline), *Somnal* (a solution of chloral hydrate and urethane in alcohol), and *Phenyl-urethane* (or Euphorine) are other preparations of the urethane class.

Urea (or Carbamide), $CO\begin{cases} NH_2 \\ NH_2 \end{cases}$, is found in human urine, in that of other mammalia, birds, reptiles, and fishes. A grown man produces about 30 gms. daily. It is the final decomposition product from the oxidation of the nitrogenous compounds in the organism. It is also found in the blood, serous fluids, aqueous humor, milk, and perspiration. It was the product of the first organic synthesis made by Wöhler in 1828, who, on evaporation to dryness of an aqueous solution of ammonium cyanate, obtained urea by molecular rearrangement: $CNONH_4 = CO\begin{cases} NH_2 \\ NH_2 \end{cases}$. It may also be formed from ammonium carbamate, from ammonia and phosgene gas, and from cyanamide and water. It may be obtained from urine by adding nitric acid, separating the crystals of urea nitrate, and decomposing these with barium carbonate. Urea forms quadratic prisms, melting at 132°, easily soluble in water and alcohol, but not in ether or chloroform. Urea forms

crystalline compounds with both bases and acids, as well as with salts.

Urea is recognized by several characteristic tests. The addition of mercuric nitrate to dilute solutions containing urea causes a white precipitate of a urea-mercuric nitrate compound; if urea crystals be touched with a drop of a concentrated aqueous solution of furfurol, and then a drop of strong hydrochloric acid, a violet color passing into purplish-violet is produced.

Urea may be determined quantitatively when in solution in several ways. First, by the aid of a standard solution of mercuric nitrate (1 c.c. of which corresponds to 0.01 gm. urea). To a measured volume of the urea solution the mercuric nitrate solution is added until all the urea has been precipitated as the double salt ($2CN_2H_4O,Hg(NO_3)_2,3HgO$) and a slight excess of mercury is in the solution. This is recognized by addition of a drop of caustic soda, which gives a yellow precipitate when the mercury is in excess, but a white one as long as urea is present in the solution. This is known as Liebig's method. Second, to the urea solution (urine) is added sodium hypobromite, and the nitrogen evolved is collected in a suitable apparatus and measured. The reaction is $CON_2H_4 + 3NaOBr = N_2 + Na_2CO_3 + NaBr + 2HBr + H_2O$. This is known as Hüfner's method.

Biuret, $C_2H_5N_3O_2$, results when urea is heated to 150°–170°, ammonia splitting off. Forms long needles, fusing at 190°. When it is dissolved in caustic soda and a little cupric sulphate is added, an onion-red to violet color is obtained, known as the "biuret reaction." This reaction is also given by peptones and by albuminoids after boiling with alkalies.

Thio-urea (Sulphurea), $CS\begin{cases}NH_2\\NH_2\end{cases}$, is formed from ammonium sulphocyanate by prolonged fusion, a molecular rearrangement taking place, $CNS.NH_4 = CS(NH_2)_2$. Heavy rhombic prisms, melting at 172°.

A derivative of sulphurea has been introduced into medicine under the name of *Thiosinamine* (Allyl-sulphurea), $CS\begin{cases}NH_2\\NH.C_3H_5\end{cases}$. It is prepared by the action of ammonia upon mustard oil (allyl sulphocyanate). Colorless or slightly yellowish crystals, fusing at 74°, with slight odor of leeks, easily soluble in water, alcohol, and ether.

Sucrol (or Dulcin), $CO\begin{cases}NH_2\\NH.C_6H_4OC_2H_5\end{cases}$.—This is urea in which a hydrogen atom is replaced by the *p-phenetol* radical (see Aromatic Compounds). This compound has been brought forward in medicine as a substitute for "saccharin," to be used for

sweetening in foods for diabetic and similar cases. It is claimed to be free from influence upon the circulation, the respiration, the nerves, and the digestive organs. 0.025 gm. of the sucrol is said to equal 5 gm. cane sugar in sweetening power.

The entrance of acid radicals in place of one or more hydrogen atoms of urea gives rise to the important classes of *Ureïdes*. When boiled with alkalies (saponified) they decompose into urea and the acid of which the radical was present. We may distinguish the two classes, *Monureïdes* and *Diureïdes*, according as one or two molecules of urea are present in combination. Of the latter class are a number of compounds which exist ready formed in the vegetable or animal kingdom, such as xanthine, hypoxanthine, theobromine, caffeine, allantoïn, and uric acid.

Hydantoïn (Glycolyl-urea), $C_3H_4N_2O_2$, belongs to the class of monureïdes. It is formed by the action of concentrated hydrogen iodide upon allantoïn. Forms needles, fusing at 215°, easily soluble in hot water.

Hydantoïc Acid (Glycoluric Acid), $C_3H_6N_2O_3$, is formed by boiling hydantoïn with baryta water or heating urea with glycocoll to 120°–125°. Forms prisms readily soluble in hot water.

Methy-hydantoïn, $C_4H_6N_2O_2$, is formed by fusing together urea and sarcosine (methyl-glycocoll), or by heating creatine with baryta water.

Methyl-hydantoïc Acid, $C_4H_8N_2O_3$, is formed by heating sarcosine and ammonium cyanate to 40°. Tablets easily soluble in warm water.

Parabanic Acid (Oxalyl-urea), $CO\begin{cases}NH—CO\\ \quad\quad|\\ NH—CO\end{cases}$. Results from the oxidation of uric acid, or direct from urea and oxalic acid in the presence of phosphorus trichloride. Broad needles which are soluble in water. On boiling with alkalies, they decompose into urea and oxalic acid.

Oxaluric Acid, $CO<^{NH_2}_{NH.CO.COOH}$, is found in small amount in human urine, and is formed by heating parabanic acid with alkalies.

Barbituric Acid (Malonyl-urea), $C_4H_4N_2O_3$, is formed by heating malonic acid and urea in the presence of phosphorus oxychloride, which acts as a dehydrating agent. Forms prisms readily soluble in hot water. Boiled with alkalies it decomposes into urea and malonic acid.

Alloxan (Mesoxalyl-urea), $C_4H_2N_2O_4$, results from the oxidation of uric acid with nitric acid. On further oxidation yields parabanic oxide and carbon dioxide. Decomposes on boiling with alkalies into mesoxalic acid and urea. Alloxan colors the skin purplish-red and imparts to it an unpleasant odor. By reduction with the aid of H_2S it is changed into *Alloxantin*, $C_8H_4N_4O_7$. This attracts oxygen from the air and changes into *Murexide* (Ammonium Purpurate), $C_8H_4(NH_4)N_5O_6$.

Alloxantic Acid (Mesoxaluric Acid), $C_4H_4N_2O_5$, is formed from alloxan by boiling with baryta water. Decomposes on boiling into mesoxalic acid and urea.

Of the Diureïdes, or compounds formed from two molecules of urea, the most important is *Uric Acid*, $C_5H_4N_4O_3$. It is found in urine. The urine of a healthy man contains daily from 0.4 to 0.8 gm. of uric acid. It is, however, especially to be found in the excrements of birds and reptiles, which often consist largely of uric acid and alkaline urates. It is wanting in normal blood, but may be present here under pathological conditions. Gouty concretions and urinary calculi are composed in part of urates. It is usually extracted from the excrement of serpents or guano by the aid of caustic soda, and the free uric acid precipitated from the filtered solution on addition of hydrochloric acid. Insoluble in cold water; difficultly soluble in hot water; insoluble in alcohol and ether. It is soluble in hot solutions of sodium phosphate and acetate, in concentrated sulphuric acid, and in glycerin. A hot, aqueous solution of lithium carbonate also dissolves it abundantly.

Salts of Uric Acid.—Uric acid is a weak, dibasic acid, and forms difficultly soluble salts. *Acid ammonium urate*, $C_5H_3(NH_4)N_4O_3$, is found frequently in calculi from the bladder and kidneys, in the urine of birds and amphibia, and in human urine as a sediment after fermentation begins. *Acid sodium urate* is a chief constituent of the excrement of serpents. It is also found as a sediment in urine, and is recognized by its brick-red color. *Acid potassium urate* is also found in urinary sediment. The most characteristic test for the recognition of uric acid is the *murexide test.* The substance is evaporated with a little nitric acid, leaving a yellowish or reddish residue. After cooling, this is moistened with a little ammonia, when the purplish-red color of murexide (acid ammonium purpurate) is developed. A drop of potassium or sodium hydrate changes this color to the blue color of the potassium or sodium purpurate.

Carnine is supposed to be dimethyl-uric acid, $C_5H_2(CH_3)_2N_4O_3$. It is found to the amount of 1 per cent. in Liebig's extract of meat.

Xanthine, $C_5H_4N_4O_2$, is found in small amount in urine and in the organs of the animal body. Also in certain plants, as in tea, malted barley, mould growths, etc. It is formed from guanine by the action of nitrous acid. Its lead compound, $C_5H_2PbN_4O_2$, is changed by the action of methyl iodide into theobromine.

Guanine (Imidoxanthine), $C_5H_5N_5O$, is found in guano and in the muscles, pancreas, spleen, liver, lungs, and retina, and in the excrement of snails, scorpions, and cephalopods. It is also found in plants, in the young sprouts of grass, oats, etc. Forms a white, chalk-like powder, insoluble in water, soluble in ammonia.

Theobromine (Dimethyl-xanthine), $C_5H_2(CH_3)_2N_4O_2$, is found in cacao beans (the fruit of *Theobroma cacao*) to the amount of 1.5 per cent. As before stated, it may also be made synthetically from xanthine. Colorless, microscopical crystals of bitter taste, subliming undecomposed at 290°–295°.

Caffeine (or Theine) is Trimethyl-xanthine, $C_5H(CH_3)_3N_4O_2$ (**Caffeina**, U.S.P.). It is found in almost all parts of the coffee-tree, the seeds containing 2 per cent. and the leaves $1\frac{1}{4}$ per cent.; in the leaves of the tea-plant; in the leaves and twigs of Paraguay tea (*maté*), and in kola nuts. Especially rich is also the guarana paste (from *Paullinia sorbilis*), containing as much as 5 per cent. Forms long needles of a silky lustre, subliming at 180° and fusing at 234–235°. Is decomposed by chlorine into dimethyl-alloxan and methyl-urea. Difficultly soluble in cold water; easily soluble in hot water and in chloroform.

Hypoxanthine (Sarcine), $C_5H_4N_4O$, is found in small amount in normal urine. Also in different organs of the body and in plants, as in yeast-cells, lycopodium, germinating seeds, etc.

Adenin (Imido-hypoxanthine), $C_5H_5N_5$, is found in the pancreas, in the spleen, and in tea-leaves. Formed also by boiling yeast with dilute sulphuric acid. The action of nitrous acid changes it into hypoxanthine.

Allantoin, $C_4H_6N_4O_3$, is found in the allantoic liquid of the cow, and in the urine of sucking calves and the urine of the dog. Results from the oxidation of uric acid.

5. Amidines of Carbonic Acid.—When the oxygen of the carbonyl group in urea is replaced by the imido group NH, we have $C(NH)<^{NH_2}_{NH_2}$. This compound is *Guanidine*, CH_5N_3. It is formed from guanine by the action of potassium chlorate and hydrochloric acid, by heating cyanamide with sal ammoniac, or most readily by heating ammonium sulphocyanate to 170°–200°.

Small amounts of it are also said to be formed when albumen is oxidized with potassium permanganate. Readily deliquescing crystalline mass, absorbing carbon dioxide from the air.

By the replacement of hydrogen atoms in guanidine by acid radicals we obtain derivatives analogous to the ureïdes derived from urea.

Glycocyamine (Guanidine-acetic Acid), $C_3H_7N_3O_2$.—Results from the addition of cyanamide to glycocoll, or from guanidine carbonate and glycocoll.

Creatine (Methyl-glycocyamine), $C_4H_9N_3O_2$, is found in the muscular juice of many animals, even invertebrates, in the blood, and in serous fluids. It may be formed also by the addition of cyanamide to sarcosine (methyl-glycocoll). Is chiefly obtained from extract of meat.

Creatinine (Anhydride of Creatine), $C_4H_7N_3O$, is formed by boiling creatine with acids. Is found also in the urine. It combines with acids and salts. A characteristic compound is that formed with chloride of zinc, difficultly soluble in water, almost insoluble in alcohol.

XII. Cyanogen and its Derivatives.

The cynogen compounds contain the monad radical $(CN)^I$. The free molecule of cyanogen, like the molecule of chlorine, must be double this atomic group.

Cyanogen, $\begin{matrix} CN \\ | \\ CN \end{matrix}$ or $(CN)_2$, is found free in the gases of blast-furnaces, and is formed when the electric spark is passed between carbon points in an atmosphere of nitrogen. May be conveniently prepared by heating oxalate of ammonium : $C_2O_4(NH_4)_2 = (CN)_2 + 4H_2O$, or by heating mercuric cyanide.

Colorless gas, with peculiar penetrating odor resembling bitter almonds. Very poisonous. It burns with a peach-red color. Is soluble in water and alcohol. These solutions become dark on standing, with separation of a brown powder known as azulmic acid, while oxalic acid, ammonia, formic and hydrocyanic acids, and urea are found in the liquid.

Paracyanogen $(CN)_x$, is a polymer of cyanogen, and is formed as a by-product when cyanogen is made from mercuric cyanide.

1. Hydrogen Cyanide and other Cyanides.—The union of the radical CN with hydrogen gives us a compound, HCN, analogous to HCl or HBr in its general chemical relations.

Hydrogen Cyanide (Prussic Acid), HCN, is a decomposition product from many organic compounds, as amygdalin of bitter almonds, etc. May be prepared by the decomposition of metallic cyanides (whether simple or double salts) with mineral acids; usually prepared thus from potassium ferrocyanide (see p. 722): $K_4Fe(CN)_6 + 5H_2SO_4 = 6HCN + FeSO_4 + 4KHSO_4$.

Is a colorless liquid, solidifying at —15° and boiling at 26.5°. It is miscible with water, and burns with a violet flame. It is a deadly poison.

When absolutely pure it can be preserved, but in the presence of traces of water or ammonia it decomposes on standing, separating out brown flocks of azulmic acid. The addition of small quantities of mineral acids renders the aqueous solution more stable. Its dilute aqueous solution is official as **Acidum Hydrocyanicum Dilutum,** U. S. P., and contains 2 per cent. by weight of absolute HCN.

Hydrocyanic acid is a weak monobasic acid, and forms numerous metallic cyanides. The most important are:

Potassii Cyanidum, U. S. P., is obtained commercially by fusion of anhydrous potassium ferrocyanide: $K_4Fe(CN)_6 = 4KCN + Fe + 2C + N_2$. Forms colorless deliquescent cubes, readily soluble in water, but only slightly so in alcohol. Usually cast in sticks or cakes. Generally contains some cyanate. Acts as a reducing agent, taking oxygen and becoming cyanate. Is used for the reduction of metallic oxides, in photography to dissolve the haloid silver salts and silver stains, and in galvanoplastic work for electro-silvering and gilding.

Argenti Cyanidum, U. S. P., forms a white powder, odorless and tasteless, turning brown on exposure to light. Insoluble in water, alcohol, or cold nitric acid. Decomposed by hot nitric acid, soluble in ammonia water, and in solutions of sodium hyposulphite and potassium cyanide.

Hydrargyri Cyanidum, U. S. P., forms colorless prisms, stable in the air, but turning dark on exposure to light. Soluble in water and alcohol. When heated in a glass tube the salt decrepitates and decomposes, giving off cyanogen gas and leaving metallic mercury.

The soluble metallic cyanides, like potassium cyanide, dissolve the insoluble cyanides, and then double cyanides are formed. There are two classes of these double cyanides, distinguished by their behavior on addition of dilute mineral acids. One class, like the double cyanides of potassium and silver, gold, zinc,

nickel, etc., break up with separation of the insoluble cyanide and liberation of hydrogen cyanide; the other class do not liberate HCN, but a complex acid, in which the CN group is combined with hydrogen and the heavy metal. Thus, $K_4Fe(CN)_6$ is potassium ferrocyanide, and on addition of dilute acid liberates $H_4Fe(CN)_6$, called hydrogen ferrocyanide, and $K_3Fe(CN)_6$, which may be taken as the equivalent of the formula of potassium ferricyanide, on addition of dilute acid liberates $H_3Fe(CN)_6$, called hydrogen ferricyanide. Similar double cyanides with the metal remaining as an integral part of the free acid are formed with manganese and cobalt.

Potassium Ferrocyanide (Yellow Prussiate of Potash), $K_4Fe(CN)_6 + 3H_2O$ (**Potassii Ferrocyanidum,** U. S. P.), is made on a large scale by fusing animal scrap, like horns and hoofs of cattle, blood, leather, etc., with potashes, and adding metallic iron. The fused mass is lixiviated with water, filtered, and crystallized. The reactions which take place may be expressed thus:

$$4C + 2N + K_2CO_3 = 2KCN + 3CO.$$
$$6KCN + FeS = K_4Fe(CN)_6 + K_2S.$$

It forms yellow crystals of the tetragonal system, easily soluble in water, insoluble in alcohol. It is not poisonous. Oxidizing agents like chlorine convert it when in solution into ferricyanide of potassium. With ferric salts it yields an insoluble blue compound, ferric ferrocyanide, known as "Prussian blue," $Fe_4(Fe(CN)_6)_3$. Other insoluble ferrocyanides are those of copper, which is brown, and zinc, which is white. Yellow prussiate of potassium is used technically in the manufacture of Prussian blue, of potassium cyanide, and of hydrogen cyanide.

Potassium Ferricyanide (Red Prussiate of Potash), $K_6Fe_2(CN)_{12}$, is produced by oxidizing the ferrocyanide in solution. Forms red, rhombic crystals, readily soluble in water. The solution gradually decomposes in the light with the formation of the yellow prussiate. In the presence of free alkali it has an oxidizing action, and is changed thereby into the yellow prussiate. With ferrous salts forms a blue precipitate, ferrous ferricyanide (Turnbull's blue).

By the action of nitric acid upon ferrocyanides are formed nitroprussides.

Sodium Nitroprusside, $Na_2Fe(CN)_5(NO) + 2H_2O$, crystallizes in red prisms, readily soluble in water. Serves as a delicate test

for soluble sulphides even in dilute solution, giving a fine but transient purplish color.

The cyanides in which an alcohol radical replaces the hydrogen of HCN form two series isomeric with each other known as the *Nitriles* and the *Isonitriles*. This isomerism is explained by the assumption that in the nitriles the atoms in the CN group are linked in one way, N≡C—, and in the isonitriles they are linked in another way, C=N—, the nitrogen being triad in the one class and pentad in the other. To the first class belong methyl cyanide or acetonitrile, $CH_3.CN$, ethyl cyanide or propionitrile, C_2H_5CN, etc. These form an homologous series, it is seen, with HCN, which might be called formonitrile. They are all poisonous liquids.

A nitro product of methyl cyanide is the very unstable *fulminic acid*, $CH_2(NO_2).CN$, the mercury salt of which is obtained when a solution of mercuric nitrate reacts with alcohol, and is known as *fulminate of mercury*. This is also explosive, and is used for percussion caps and for fuses to explode dynamite cartridges.

The Isocyanides or Isonitriles differ in many respects from the corresponding cyanides. They are liquids of extremely sickening odor, but are *not* poisonous like the cyanides. They are sometimes called *carbylamines*, as $CH_3.NC$, methyl isocyanide, or methyl carbylamine. The production of one of this class, phenyl carbylamine, when chloroform is heated with aniline and alcoholic potash, was given as a test under Chloroform (see p. 622).

2. Cyanic and Cyanuric Acids.—By the replacement of an H atom in HCN by the group OH we obtain CN.OH. This compound is not known in the free state, but only in its esters. The isomeric compound, CO.NH, however, is known as *Isocyanic Acid*, a very unstable, volatile liquid, which readily polymerizes, and yields Cyanuric Acid, $(CONH)_3$, and *Cyamelide*, $(CONH)_x$.

Potassium Isocyanate (commonly called Cyanate), CONK, is obtained by fusing potassium cyanide or yellow prussiate of potash with metallic lead or manganese peroxide. Forms white scales, easily soluble in water and alcohol.

Ammonium Isocyanate (commonly called Cyanate), $CON.NH_4$, is a white, crystalline mass, which changes on heating into the isomeric compound urea, $CO\begin{cases}NH_2\\NH_2\end{cases}$. (See p. 715.)

3. Sulphocyanic and Isosulphocyanic Acids.—Corresponding to cyanic and isocyanic acids are the sulphur compounds

N≡C—SH, sulphocyanic acid, and CS.NH, isosulphocyanic acid. The metallic salts are derivatives of the first of these.

Potassium Sulphocyanate, CNSK, is readily obtained by fusing ferrocyanide of potassium with sulphur and potash. Colorless, deliquescent prisms, soluble in water, with considerable lowering of temperature.

Ammonium Sulphocyanate, $CN.SNH_4$, is obtained by the action of carbon disulphide upon concentrated ammonia in alkaline solution. Colorless, deliquescent prisms, easily soluble in water. These sulphocyanates are used as reagents to distinguish ferric from ferrous solutions, giving with the former blood-red coloration, while remaining colorless with the latter.

Mercuric Sulphocyanide, $(CN.S)_2Hg$, is a white, insoluble powder. When heated, swells up enormously as it is decomposed. Used in toys known as "Pharaoh's serpents."

Of the esters two series are known, the Sulphocyanates and the Isosulphocyanates. To the first class belong *Ethyl Sulphocyanate*, $CN.SC_2H_5$, and *Allyl Sulphocyanate*, $CN.SC_3H_5$. This latter is the starting-point in the manufacture of artificial mustard oil. By the action of allyl iodide on an alcoholic solution of potassium sulphocyanate this sulphocyanate of allyl is made. It is then distilled, when, by molecular rearrangement, it becomes *Allyl Isosulphocyanate*, $CS.NC_3H_5$, or true mustard oil (**Oleum Sinapis Volatile**, U. S. P.). It is also obtained from the seeds of the black mustard by distillation with water. It forms a liquid slightly soluble in water, of irritating odor, inciting to tears and producing blisters upon the skin. Boils at 151°.

The esters of isosulphocyanic acid are often known collectively as "mustard oils." Thus, we have *methyl-mustard oil*, $CS.NCH_3$; *ethyl-mustard oil*, $CS.NC_2H_5$; *n-propyl-mustard oil*, $CS.NC_3H_7$

4. Amides of Cyanogen.—The only important compound in this series is *Cyanamide*, $CN.NH_2$. May be formed by the action of ammonia upon cyanogen chloride in ethereal solution. Colorless, deliquescent crystals, easily soluble in water, alcohol, and ether. By the action of dilute acids it takes up the elements of water and becomes urea: $CN.NH_2 + H_2O = CO\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.$, and in analogous manner it takes up H_2S and becomes sulphurea, $CS\left\{\begin{matrix}NN_2\\NH_2\end{matrix}\right.$. When heated with ammonia salts it yields salts of guanidine (see p. 719).

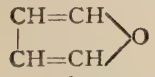
CHAPTER IV.

CLOSED-CHAIN GROUPS WITH LESS THAN SIX CARBON ATOMS.

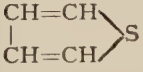
THE compounds thus far considered were all derivatives of methane and the similar hydrocarbons, which, whether saturated or unsaturated, had the one feature in common, that they were *open-chain* hydrocarbons; that is, aggregates of carbon atoms linked together in such a way that the end carbon atoms were distinguished from those occupying a middle position in the molecular grouping.

For benzene and the so-called "aromatic compounds," on the other hand, we must assume that the molecule contains six carbon atoms linked together in a closed chain, so that no one of the six is an end carbon atom. The presumptions in favor of this theory will be stated in the next chapter. As transition compounds from the open-chain compounds to the true aromatic compounds or benzene derivatives may be noted three compounds which show a closed-chain structure in which less than six carbon atoms are present. These are *Furfurane* (or *Furane*), C_4H_4O, *Thiophene*, C_4H_4S, and *Pyrrol*, C_4H_4NH. Of these, the first is most nearly related to the methane derivatives, being formed in many cases in the decomposition of the sugars and carbohydrates, and the other two accompany benzene in the products of destructive distillation, and more nearly resemble the true aromatic compounds. The structural formulas given to the three compounds show a close similarity and relationship, and the fact that all three may be derived from the same compounds by three different reactions goes to establish this relationship.

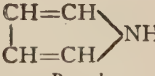
The formulas ascribed to them are:



Furfurane.



Thiophene.



Pyrrol.

All three are liquids, boiling at relatively low temperatures,—furfurane at 32°, thiophene at 84°, and pyrrol at 130°.

All three are insoluble, or only slightly soluble, in water, but easily soluble in alcohol and ether. They show analogous color reactions. All three give blue or violet coloring matters with

isatin and sulphuric acid ; the vapor of pyrrol colors a pine shaving that has been moistened with HCl carmine-red (whence the name, from πυρρός, fiery-red), while furfurol vapor colors it an emerald-green.

All three are derived from mucic acid by different reactions. Mucic acid destructively distilled yields first pyromucic acid (furfurane-carboxylic acid), $C_4H_3O(COOH)$, and this on further heating splits off CO_2, and yields furfurane ; by the dry distillation of ammonium pyromucate is obtained pyrrol ; and by the action of hydrogen sulphide upon pyromucic acid is formed thiophene.

Similarly all three are derived from acetonyl-acetone by different reactions, and both pyrrol and thiophene from succinic acid by the action of different reagents.

1. Furfurane and its Derivatives.—*Furfurane* (or *Furane*), C_4H_4O, is formed by the distillation of pine wood. Is a colorless, mobile liquid of chloroform-like odor, boiling at 32°. It is recognized by the emerald-green color which it imparts to a pine shaving which has been moistened with hydrochloric acid. Besides furfurane, methyl-furfurane appears to be present also in pine-wood tar.

Furfurol (Furfurane Aldehyde), $C_4H_3O.COH$, results from the oxidation of the sugars with manganese dioxide and sulphuric acid, as well as from the distillation of the pentoses, bran, sawdust, starch, gum arabic, etc., with sulphuric acid. It is contained in beer and in fusel oil, and hence in brandy. It is also a decomposition product of the albuminoids. It is a colorless oil of agreeable odor, resembling that of bitter almonds, turning brown in the air. As an aldehyde it reduces ammoniacal silver solution.

Pyromucic Acid, $C_4H_3O.COOH$, is the acid corresponding, and is produced by the oxidation of furfurol as well as in the dry distillation of mucic acid. Needles or plates, melting at 134°, resembling benzoic acid in appearance.

2. Thiophene and its Derivatives.—*Thiophene*, C_4H_4S, accompanies benzene, C_6H_6, in coal-tar, and is only separated from it with difficulty. Its homologues likewise accompany those of benzene, displaying nearly the same boiling points and many similar reactions. It is separated from the crude benzene of coal-tar by shaking out with successive quantities of concentrated sulphuric acid, in which it is soluble. Is a liquid of weak odor, boiling at 84°. The most delicate test for it is the blue color due

to the formation of indophenin, obtained on shaking a solution containing it with sulphuric acid and isatin.

Two thiophene derivatives have been recommended for use in medicine :

Thiophene Diiodide, $C_4H_2I_2S$, and *Sodium Thiophene-sulphonate*, $C_4H_3S.SO_3Na$.—The former, which is recommended as a substitute for iodoform, is in colorless, readily volatile crystals, melting at 40.5° C. The odor is aromatic but not unpleasant. It is insoluble in water, but easily soluble in ether, chloroform, and in hot alcohol. It contains 75.5 per cent. of iodine and 9.5 per cent. of sulphur. The second compound is a white, crystalline powder, recommended for use in salve in cases of prurigo.

3. Pyrrol and its Derivatives.—*Pyrrol*, C_4H_4NH, is obtained in the dry distillation of bones and in coal-tar. It is a liquid, boiling at 130°, and smelling like chloroform. Is insoluble in water and alkalies, soluble in alcohol, ether, and dilute acids.

Tetraiodopyrrol (*Iodol*), C_4I_4NH.—When iodine in alcoholic solution acts upon pyrrol, especially in the presence of an alkali, a substitution compound, to which the name of iodol has been given, separates out in a yellow, crystalline powder, insoluble in water, soluble in alcohol. It is used as an odorless substitute for iodoform, and is especially characterized by its high percentage of iodine (88.97 per cent.).

Antipyrin (*Phenyl-dimethyl-pyrazolon*), $C_{11}H_{12}N_2O$.—By the action of phenyl-hydrazine, $C_6H_5.NH.NH_2$, upon aceto-acetic ether (see p. 667) water and a molecule of alcohol are split off, and a compound is obtained which is called phenyl-methyl-pyrazolon. This would be a derivative of a base called pyrazol, $\begin{matrix}CH{=}N\\ |\quad\quad\\ CH{=}CH\end{matrix}\!\!>\!NH$, a compound differing from pyrrol only in the substitution of the nitrogen atom for the triad group CH. In the phenyl-methyl-pyrazolon we would have besides the substitution of the radicals phenyl and methyl the change of a CH group for the dyad group CO, making its structural formula $\begin{matrix}(CH_3)C{=}N\\ |\quad\quad\\ CH_2{-}CO\end{matrix}\!\!>\!N(C_6H_5)$. When this is methylated by the action of methyl iodide, there is formed the hydrogen iodide compound of the new base phenyl-dimethyl-pyrazolon, which possesses the structural formula $\begin{matrix}(CH_3)C{-}N(CH_3)\\ \|\quad\quad\\ CH{-}CO\end{matrix}\!\!>\!N(C_6H_5)$.

The free base comes into commerce as a white, crystalline powder, melting at 113°, almost odorless, easily soluble in water, alcohol, chloroform, difficultly soluble in ether. As a base it forms addition salts with the acids like ammonia. It shows two characteristic color reactions: with ferric chloride it is colored deep red, which color is changed by sulphuric acid into bright yellow; with nitrous acid a green color, and in concentrated solutions a separation of green crystals of isonitroso-antipyrin, $C_{11}H_{11}N_3O_2$. Both these reactions are adapted for the recognition of antipyrin in urine. Antipyrin is probably the best known of the newer synthetic remedies.

Antipyrin Salicylate (Salipyrin), $C_{11}H_{12}N_2O.C_7H_6O_3$, forms a colorless, crystalline powder, melting at 92°. Used as an antineuralgic remedy.

Iodo-pyrin (Iodo-antipyrin), $C_{11}H_{11}IN_2O$, forms lustrous, colorless, prismatic needles, difficultly soluble in cold water, more readily in hot water. Melts at 160°.

Naphtho-pyrin (β-naphtol-antipyrin) is a molecular combination of β-naphtol and antipyrin. Recently introduced into medicine.

Monochloral-antipyrin (Hypnal) and *Bichloral-antipyrin* have been mentioned under Chloral-hydrate (see p. 645).

Tolypyrin (Tolyl-dimethyl-pyrazolon), $C_{12}H_{14}N_2O$, is a homologue of antipyrin. Made by using instead of phenyl-hydrazine the homologous compound *p*-tolyl-hydrazine in the reaction with aceto-acetic ether. Colorless crystals, fusing at 136°–137°, soluble in water and alcohol, difficultly soluble in ether. Shows the same color reaction with ferric chloride and nitrous acid as antipyrin.

Tolypyrin Salicylate (Tolysal), $C_{12}H_{14}N_2O.C_7H_6O_2$, is formed by the direct union of the two components. Is in every way analogous to antipyrin salicylate.

CHAPTER V.

CLOSED-CHAIN OR AROMATIC COMPOUNDS (CYCLIC HYDROCARBONS AND DERIVATIVES).

In studying the methane derivatives we had several series of hydrocarbons, of which that containing the maximum hydrogen in any given case for the amount of carbon present was called the Paraffin series, and had assigned to it the general formula C_nH_{2n+2}. This series was also termed the saturated series of hydrocarbons, because no addition compounds could be formed. The explanation of this fact and the verification of the general formula just stated were both found in the structural formulas, showing an open-chain formation with single linking of adjacent carbon atoms. The other series of hydrocarbons, with the general formulas C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-4}, and C_nH_{2n-6}, respectively, were all unsaturated hydrocarbons and ready to unite directly with halogen atoms and atomic groups to form addition compounds. The explanation of this fact was also given in the structural formulas, which showed an open-chain formation, but with double and treble linking between certain of the carbon atoms. This form of linking was seen to be unstable, and hence the tendency to pass into saturated compounds with an open-chain structure and single linking of the carbon atoms.

We meet, however, in the Benzene series of hydrocarbons, which are the products of the distillation of many complex substances, and which are found to be the fundamental substances of an immense number of compounds occurring in the vegetable kingdom, hydrocarbons of the general formula C_nH_{2n-6}, which are relatively stable and more like saturated than unsaturated hydrocarbons. While it is true that addition of halogen atoms may be effected within certain limits, these compounds do not tend to form as readily as substitution compounds, in which the hydrogen atoms of the original hydrocarbons are readily replaced by halogens and radicals like methyl and ethyl.

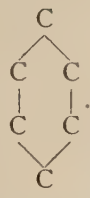
The fundamental hydrocarbon of this series is benzene, C_6H_6, and the homologues are formed by the replacement of one or more

of these six hydrogen atoms by methyl and ethyl groups. The limit of this replacement is reached, of course, when six hydrogen atoms have been exchanged for other atoms or atomic groups. Both the hydrocarbons of this series and the substitution derivatives are more stable than the addition compounds before referred to. Moreover, all the derivatives of benzene can be converted either into benzene itself or into very nearly allied compounds by relatively simple reactions. Benzene is, then, in a peculiar degree both the starting-point and the basis of the compounds connected with it.

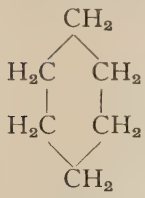
It is obvious, then, that benzene and its homologous hydrocarbons must be differently constituted structurally from the paraffin series or any of the unsaturated series that are convertible into methane derivatives by addition. The benzene derivatives are not convertible into marsh-gas derivatives by addition of halogen or other atomic groups ; benzene, C_6H_6, cannot be converted into hexane, C_6H_{14}, by any means, direct or indirect. As stated before, addition compounds can be formed. We can obtain $C_6H_6Cl_6$ and from this C_6H_{12}, but the addition of hydrogen stops there. It is strikingly evident, from this and many similar observations, that C_6H_6 is a peculiarly-constituted molecule, which resists change and remains substantially intact through all the substitutions that may be effected. We cannot transform it into a simpler molecule containing 5, 4, or 3 carbon atoms ; when oxidized, which is only accomplished with difficulty, it goes into carbon dioxide and water.

1. Theories as to the Structure of the Benzene Molecule.—The theory as to the constitution of the benzene molecule which has found general acceptance is that of Kekulé, first published in 1866. This not only explains known facts with regard to benzene and its thousands of derivatives, but has found confirmation in the discovery and preparation of the immense numbers of so-called "coal-tar" products which are chemically grouped and classified by its aid. According to this theory the six carbon atoms are linked together in such a way as to form a *closed chain*. We may arrange them in a continuous chain of which the two ends are connected together, but there is no reason here for making it a longitudinal chain. Therefore the six carbon atoms may be considered as placed at equal distances apart on the circumference of a circular ring, or in any other position that might be assumed by a closed chain of six units, but for convenience in writing the hexagon figure is usually

chosen. The benzene molecule would then show as its frame-

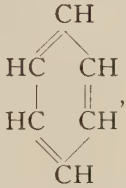


work . Each of these carbon atoms has attached to it one atom of saturating hydrogen in the formula C_6H_6. If each carbon atom had two hydrogen atoms attached we would have

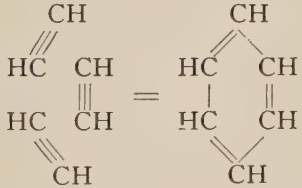


or C_6H_{12}, and it is obvious that the four bonds of tetrad carbon would be satisfied.

But C_6H_6 is the formula of the stable molecule and not C_6H_{12}. The latter readily gives up six atoms of hydrogen on oxidation. Kekulé, therefore, considers that each carbon atom in the benzene molecule is linked doubly with one other carbon. This would make an alternate single and double linking, as shown in the formula

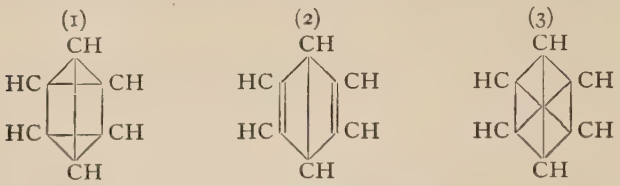


, and chemists have generally adopted this graphic expression for the benzene molecule. This formula agrees very well with the formation of benzene from acetylene, H—C≡C—H, three molecules of the latter uniting at a low red heat to form one molecule of benzene, or the formation of mesitylene (trimethyl-benzene)



from acetone (see p. 647) when the latter is distilled with dilute sulphuric acid. It also explains the capability of benzene and its derivatives to form addition compounds up to a certain limit. As, however, no experimental proof of this particular structural formula can be given, other formulas have been proposed, such as those of

(1) Claus and Koerner, (2) Dewar, and (3) Ladenburg. None of these, however, explains all the observed reactions of benzene



and its derivatives as well as the structural formula originally proposed by Kekulé.

2. Formation of Benzene Homologues.—In the case of open-chain hydrocarbons, whether of the saturated or unsaturated series, the successive homologues were formed by lengthening the chain or adding on additional carbon atoms with the requisite saturating hydrogen. Thus, following methane we had ethane, propane, butane, etc., and following ethylene we had propylene, butylene, etc. In the case of benzene the closed-chain structure precludes this method of forming an homologous series. But we have following benzene, C_6H_6, toluene, C_7H_8, xylene, C_8H_{10}, etc., as far as $C_{12}H_{18}$. A slight examination of these compounds, as, for example, with oxidizing agents, shows that there are two parts in them of very different stability, a *nucleus*, C_6H_5 or C_6H_4, not oxidizable, and one or two *side-groups*, CH_3, which have replaced hydrogen atoms of the original C_6H_6, and are easily oxidized to COOH groups. In other words, toluene is methyl-benzene, xylene is dimethyl-benzene, etc., and their formulas may be written $C_6H_5.CH_3$ and $C_6H_4(CH_3)_2$, etc., up to hexamethyl-benzene, $C_6(CH_3)_6$, when this series of homologues stops. It is true we can have ethyl-benzene and diethyl-benzene or methyl-propyl-benzene and similar derivatives, but these are not found in any great number in nature. Nor are their derivatives of the same importance as those of the methylated benzenes.

3. Differences between the Benzene Hydrocarbons and the Open-Chain Hydrocarbons.—(*a*) We notice first that the action of concentrated nitric acid is quite different. With the closed-chain hydrocarbons a hydrogen atom of the nucleus is readily replaced by the group NO_2, as $C_6H_6 + NO_2.OH = C_6H_5.NO_2 + H_2O$, the product being called nitrobenzene. With paraffin hydrocarbons nitric acid has little or no action, even when heated for a time.

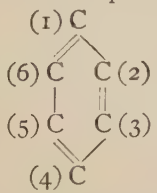
(*b*) With concentrated sulphuric acid the benzene hydrocar-

bons give rise to sulphonic acids, as $C_6H_6 + SO_3H.OH = C_6H_5(SO_3H) + H_2O$, the product being called benzene-sulphonic acid. Concentrated sulphuric acid has no action on the paraffin hydrocarbons, and with the olefines it forms addition compounds without displacement of hydrogen.

(*c*) As mentioned before, under the influence of oxidizing agents the homologues of benzene are easily oxidized, yielding the corresponding carboxylic acids. Thus, toluene, $C_6H_5—CH_3$, is oxidized by dilute nitric acid or by chromic acid to benzoic acid, $C_6H_5.COOH$. The open-chain hydrocarbons are only acted upon by oxidizing agents with great difficulty.

(*d*) The hydroxyl derivatives like $C_6H_5.OH$ are quite different from the simple OH derivatives of the paraffin or other open-chain hydrocarbons. The former have more of an acid character, while the latter are basic hydrates. Thus, C_6H_5OH is phenol or carbolic acid, while $C_2H_5.OH$ is ethyl alcohol, which forms esters or salts with the acids.

4. Isomerism in the Closed-Chain Hydrocarbons.—In the hydrocarbons of the paraffin series it is possible to obtain isomeric mono-substitution derivatives, as, for example, normal propyl chloride, $CH_2Cl.CH_2.CH_3$, and isopropyl chloride, $CH_3.CHCl.CH_3$; in the case of benzene, isomeric mono derivatives *cannot* be obtained. The six hydrogen atoms of the benzene seem to possess an equal value. It is a closed-chain structure, and it matters not at what point in the ring thus formed the single substitution takes place. This fact has been proved experimentally. It is different when two atoms of hydrogen in the benzene molecule are replaced by other atoms or groups. These di-substitution derivatives may exist in three isomeric modifications. We may have three dichlor-benzenes, three dimethyl-benzenes, three dinitro-benzenes, etc. This also has been established experimentally, and the limit set at three.

If we now look at the benzene molecule as figured in Kekulé's theory, we see the explanation of this fact. Taking the structural formula 

, and numbering the carbon atoms from the top going to the right, we have for the purpose of representation each one indicated. Now, if the replacement take place at

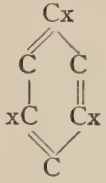
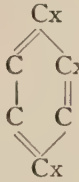
(1) and (2), or (2) and (3), or (3) and (4), or (4) and (5), or (5) and (6), or (1) and (6), the resulting di-substitution compound is one and the same substance. While we figure this hexagon structure for convenience of explanation of the observed characters of benzene, we do not for one moment pretend that it has a fixed position in space with a north and a south corner, or with two eastern and two western carbon atoms. But in the cases just mentioned *the substitution has taken place in connection with adjacent or directly connected carbon atoms.* To distinguish them all such di-substitution compounds are called *ortho* compounds, as ortho-dichlor-benzene. If the replacement take place at the carbon atoms marked (1) and (3), or (2) and (4), or (3) and (5), or (4) and (6), or (5) and (1), or (6) and (2), the resulting di-substitution compound is one and the same substance. In these cases *the substitution has taken place in connection with carbon atoms separated by one intervening carbon atom.* Such compounds are called *meta* compounds, as meta-dimethyl-benzene. If the replacement take place at the carbon atoms marked (1) and (4), or (2) and (5), or (3) and (6), the resulting di-substitution compound is one and the same substance. In these cases *the substitution has taken place in connection with carbon atoms separated by two intervening carbon atoms.* Such compounds are called *para* compounds, as para-dinitro-benzene. Frequently these designations are indicated by the initials only, as *o*-oxybenzoic acid, *m*-xylene, and *p*-phenol-sulphonic acid.

When three hydrogen atoms of the benzene molecule are replaced the case becomes more difficult. We may have three contingencies to consider here: (1) all three substituting atoms or groups are alike; then three isomers may exist; (2) of the substituting elements two are alike and the third is different; in this case six isomers may form; (3) if all three substituting elements are different, ten isomers may form.

When more than three substitutions take place, the number of isomers becomes very great.

In distinguishing between the different tri- and tetra-substitution derivatives, at times the designations *v* (standing for *vicinus*, neighboring), *s* (standing for symmetrical), and *a* (standing for asymmetrical) are used. Thus,

would indicate a **tri-**

substitution derivative which would be marked *v*, as *v*-trinitro-benzene, while the figures  and  would be designated by the *s* and *a* respectively, as *s*-trimethyl-benzene and *a*-trichlor-benzene.

These cases of isomerism, it will be noticed, are all concerned with the position in the nucleus assumed by the replacing atom or group. We may also have side-group isomerism, as normal propyl-benzene and isopropyl-benzene.

More important than this last, however, is the case where a substituent enters the benzene nucleus in one case and the side-group in another case, giving us the so-called "mixed isomerism." Thus, $C_6H_4Cl.CH_3$, monochlor-toluene, and $C_6H_5CH_2Cl$, benzyl chloride, or $C_6H_4(CH_3)_2$, xylene, and $C_6H_5.C_2H_5$, ethyl-benzene, are isomeric.

The determination of the nature of a di-substitution derivative of benzene, whether ortho, meta, or para, is to be accomplished by the treatment with reagents, whereby the nature of the side-group may be changed and the product studied as to its properties. Ortho derivatives through a series of such changes will remain ortho derivatives, and so with the meta and the para compounds. By such a series of transformations it becomes possible correctly to identify the nature of the original compound.

CHAPTER VI.

AROMATIC COMPOUNDS CONTAINING ONE NUCLEUS.

In explaining the theories held as to the fundamental differences between the aromatic compounds and the open-chain hydrocarbons and their derivatives, we have touched only upon the structure of benzene, taking it as the type of closed-chain compounds, and, in fact, the starting-point from which they are derived. We will see, however, later, that two or more of these benzene nuclei may unite, either by simple linking without condensation, or by condensing together to form a compound nucleus, obviously related to the simpler benzene molecule, but built up by its doubling or trebling itself. Thus, diphenyl, diphenyl-methane, triphenyl-methane, and indigo all represent aromatic compounds with more than one benzene nucleus in which the parts are linked together without condensation of the nuclei. On the other hand, naphthalene, anthracene, phenanthrene, quinoline, and acridine all represent molecules formed by the condensation of benzene nuclei.

We shall first confine our attention to those aromatic compounds in which a single benzene nucleus appears as the basis of the molecule.

I. Hydrocarbons.

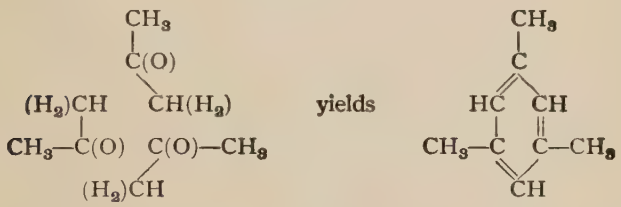
1. Saturated Hydrocarbons.—We have here to deal with benzene and its homologues. They occur to some extent in the free state in nature, being found in Galician and Hanoverian petroleum, and even in small amount in Pennsylvania petroleum. They are obtained, however, most abundantly as the product of the destructive distillation of bituminous coal, and hence are contained in coal-tar. This is a very complex mixture, and more than forty distinct compounds of the aromatic class have been identified in it. When roughly fractioned from the tar-stills it yields three main fractions: (1) The light oil, sp. gr. 0.9, boiling point up to 150°, which contains mainly benzene and its homologues, with some naphthalene; (2) middle oil, sp. gr. up to 1.01, boiling point 150° to 210°, which contains especially naphthalene, carbolic and cresylic acids, and quinoline bases; and (3) heavy oil, sp. gr.

up to 1.04, boiling point from 210° to 300°, containing chiefly anthracene and phenanthrene.

From the first of these fractions, by careful fractionating with the aid of column stills, the benzene hydrocarbons may be obtained. Their separation, however, is not entirely possible by fractional distillation alone, but requires special treatment with reagents.

Benzene derivatives can be formed from bodies of the methane series by a number of reactions, some of which may be noted.

The vapors of alcohol when led through a red-hot tube yield benzene. Acetylene polymerizes at a low red heat, three molecules uniting to form one molecule of benzene. This has been illustrated graphically (see p. 731). Allylene, C_3H_4, in the same way polymerizes to form mesitylene or trimethyl-benzene, C_9H_{12}, when distilled with dilute sulphuric acid. Ketones condense to benzene hydrocarbons when distilled with dilute sulphuric acid. Thus, acetone yields mesitylene:



Hexyl iodide, $C_6H_{13}I$, can be converted into hexachlor-benzene, C_6Cl_6, by heating it with ICl_3, and into hexabrom-benzene, C_6Br_6, by heating the hexyl iodide with bromine at 260°.

Mellitic acid, $C_6(COOH)_6$, is produced by the oxidation of graphite or lignite by means of potassium permanganate.

Potassium carboxide, $C_6(OK)_6$, which is formed by the action of carbon monoxide upon potassium, is the potassium compound of hexoxy-benzene, $C_6(OH)_6$.

These methods, however, may be said to be isolated reactions, and not used as general methods for their production. Among the general methods may be mentioned:

1. By treating a mixture of brominated hydrocarbon and methyl or ethyl iodide with sodium in ethereal solution: $C_6H_5Br + CH_3I + Na_2 = C_6H_5.CH_3 + NaI + NaBr$.

2. By the action of methyl chloride upon benzene or its homologues in the presence of aluminum chloride: $C_6H_6 + 2CH_3Cl = C_6H_4(CH_3)_2 + 2HCl$.

3. The benzene hydrocarbons result from their respective carboxylic acids by distilling them with soda-lime : $C_6H_5.COOH = C_6H_6 + CO_2$.

4. From sulphonic acids by the separation of the SO_3H group : $C_6H_4(CH_3)SO_3H + H_2O = C_6H_5(CH_3) + H_2SO_4$.

5. By distillation of the phenols with zinc-dust.

The general characters of the benzene hydrocarbons that seem most important are :

1. They may all be distilled without decomposition. Most of them are colorless liquids of peculiar aromatic odor. Durene, penta- and hexamethyl-benzene are crystalline solids at ordinary temperatures.

2. As before stated, they readily form nitro and sulphonic derivatives.

3. Benzene oxidizes with some difficulty to oxalic, formic, and carbonic acids ; the aromatic hydrocarbons with side-groups are readily oxidized to acids, as $C_6H_4(CH_3)_2 = C_6H_4(COOH)_2$.

4. By reduction with hydrogen iodide under pressure at high temperatures the benzene hydrocarbons add on hydrogen up to the limit of six atoms.

5. The halogens form with benzene in sunlight addition compounds like $C_6H_6Cl_6$. On the other hand, in diffused daylight they form substitution compounds like C_6H_5Cl.

The most important of the benzene hydrocarbons are shown arranged in tabular form on the next page.

Benzene, C_6H_6, was discovered by Faraday in 1825, and detected in coal-tar by Hofmann in 1845. It is practically always obtained from the light oil of tar by taking the purified fraction boiling at 83°–85° and chilling it, when the benzene will crystallize out from the adhering portions of higher homologues. It is also obtainable from illuminating gas, or perfectly pure by distilling benzoic acid with lime. It has a melting point of 5.4°, and a boiling point of 80.5°. Sp. gr. at 0° 0.9. It burns with a luminous but smoky flame. It is an excellent solvent for fats, resins, iodine, sulphur, and phosphorus. Commercial benzene generally contains thiophene, and hence gives the indophenin reaction (see p. 727). Is used on a large scale as the starting-point for the manufacture of aniline and other technical products of value in the color industry.

Toluene (Methyl-benzene), $C_6H_5.CH_3$, is formed by the distillation of certain resins, as Tolu balsam (whence the name), dragon's-blood, etc. Is generally obtained along with benzene

BENZENE SERIES, SATURATED HYDROCARBONS. GENERAL FORMULA, C_nH_{2n-6}.

C_6H_6	C_6H_6, Benzene, boiling point 80.4°.			
C_7H_8	$C_6H_5.CH_3$, Toluene, boiling point 111°.			
C_8H_{10}	$C_6H_4(CH_3)_2$, Xylenes: *o*- b. p. 142°, *m*- b. p. 139°, *p*- b. p. 137°.	$C_6H_5(C_2H_5)$, Ethyl-benzene, boiling point 134°.		
C_9H_{12}	$C_6H_3(CH_3)_3$, Trimethyl-benzenes: *s*- = Mesitylene, b. p. 163°. *a*- = Pseudo-cumene, b. p. 169°. *v*- = Hemellithene, b. p. 175°.	$C_6H_4(CH_3)(C_2H_5)$, Methyl-ethyl-benzenes, or Ethyl-toluenes: *o*- b. p. 160°, *m*- b. p. 159°, *p*- b. p. 162°.	$C_6H_5(C_3H_7)$, Normal propyl-benzene, b. p. 157°. Isopropyl-benzene (cumene), b. p. 153°.	
$C_{10}H_{14}$	$C_6H_2(CH_3)_4$, Tetramethyl-benzenes: *s*- = Durene, m. p. 79°, b. p. 190°. *a*- = Isodurene, b. p. 195°. *v*- = Prehnitene, m. p. −4°, b. p. 204°.	$C_6H_3(CH_3)_2(C_2H_5)$, Dimethyl-ethyl-benzenes. Six isomers possible.	$C_6H_4(C_2H_5)_2$. Diethyl-benzenes (3). $C_6H_4(CH_3)(C_3H_7)$. Cymene, b. p. 176°. Six isomers possible.	$C_6H_5(C_4H_9)$, Butyl-benzenes. Four isomers possible.
$C_{11}H_{16}$	$C_6H(CH_3)_5$, Pentamethyl-benzene, m. p. 51°, b. p. 231. $C_6H_5(C_5H_{11})$, Amyl-benzene, etc.			
$C_{12}H_{18}$	$C_6(CH_3)_6$, Hexamethyl-benzene, m. p. 164°, b. p. 264. $C_6H_3(C_2H_5)_3$, Triethyl-benzene, etc.			

in the light oil of tar. It can also be made synthetically, as mentioned under general modes of formation (see p. 737). It is very similar to benzene, and when obtained from coal-tar is often contaminated with thiotolene (methyl-thiophene). Toluene boils at 111°, and is still liquid at —28°. Oxidized by nitric or chromic acid it yields benzoic acid. Is less poisonous, taken internally, than benzene. It is changed into benzoic acid in the organism, and eliminated from the system as hippuric acid.

Xylenes (Dimethyl-benzenes), $C_6H_4.(CH_3)_2$.—The xylene of coal-tar is a mixture of the three isomers, meta-xylene making up 70 to 85 per cent. of it. The boiling points lie so close (142°, 139°, 137°) that they cannot be separated by fractional distillation. As *m*-xylene is oxidized more slowly than its isomers, it can be separated in this way. The others are separated by converting them into sulphonic compounds. When oxidized they yield the corresponding isomeric phthalic acids.

Ethyl-benzene, $C_6H_5.C_2H_5$, has been made synthetically from brom-benzene and ethyl iodide in the presence of Al_2Cl_6. Boils at 134°. When oxidized yields benzoic acid.

Mesitylene (1:3:5 Trimethyl-benzene), $C_6H_3(CH_3)_3$, is contained in coal-tar along with the other two isomeric trimethyl-benzenes. It can also be prepared from acetone or allylene (see page 737). It is a liquid of agreeable odor. Nitric acid oxidizes the side-groups one by one, producing successively a monobasic, a dibasic, and a tribasic acid.

Cumene (Isopropyl-benzene), $C_6H_5(C_3H_7)$, is produced by the distillation of cumic acid with lime as well as synthetically. Boils at 153°.

Durene (Tetramethyl-benzene), $C_6H_2(CH_3)_4$, has been found in coal-tar, and can be made from toluene and methyl chloride in the presence of Al_2Cl_6. It is a solid, melting at 79°, and possesses a camphor-like odor.

Cymene (Methyl-propyl-benzene), $C_6H_4(CH_3)(C_3H_7)$.—It is found in Roman cumin oil, as well as in eucalyptus and thyme oils, and results upon heating camphor with P_2O_5 and P_2S_5. It is a liquid of agreeable odor, boiling at 176°.

2. Unsaturated Hydrocarbons.—The unsaturated hydrocarbons of the aromatic series are formed by the entrance of the benzene radicals (phenyl) into the unsaturated hydrocarbons of the methane series. Thus, by the replacement of a hydrogen atom of ethylene, $CH_2=CH_2$, we obtain $C_6H_5.CH=CH_2$, Phenyl-ethylene or Styrene, and by the replacement of a hydro-

gen atom in acetylene, $CH{\equiv}CH$, we obtain $C_6H_5.C{\equiv}CH$, Phenyl acetylene.

Styrene (Phenyl-ethylene), $C_6H_5.CH{=}CH_2$, is found in storax (**Styrax**, U.S.P.), from the bark of *Liquidambar orientalis*, and in small amount in coal-tar. May be made synthetically by passing a mixture of benzene and ethylene through red-hot tubes, or by the heating of cinnamic acid with water to 200°. Aromatic-smelling liquid, boiling at 144°. It is optically inactive.

Phenyl-acetylene, $C_6H_5.C{\equiv}CH$, may be prepared by heating styrene bromide, $C_8H_8Br_2$, with potash: $C_8H_8Br_2 + 2KOH = C_8H_6 + 2HBr + 2H_2O$; also by the splitting off of CO_2 from phenyl-propiolic acid, $C_6H_5.C{\equiv}C.COOH$. Pleasant-smelling liquid, boiling at 139°. Shows its character as an acetylene derivative by combining with silver and cuprous solutions to form explosive metallic compounds.

These unsaturated hydrocarbons, like the ethylene and acetylene series, combine directly and easily with the halogens to form addition compounds.

3. Hydrogen Addition Compounds of the Benzene Series.—We have already stated that benzene and its homologues, by prolonged treatment with HI under pressure, can be made to take up six hydrogen atoms. The addition hydrocarbons so obtained have sometimes been called the "naphthenes," and, although isomeric with the olefines, differ from them notably. For instance, they are not attacked by alkaline permanganate solution, do not dissolve in sulphuric acid, and are not able to add on bromine. They are found in considerable quantity in Russian petroleum, and in smaller amount in other oils. They very readily yield to oxidizing agents, and give up the six atoms of extra hydrogen.

II. The Halogen Derivatives of the Benzene Hydrocarbons.

The halogen derivatives of these hydrocarbons are formed by substitution. With benzene, these derivatives are entirely analogous to the halogen substitution derivatives of methane and its homologues, $C_6H_5.Cl$, monochlor-benzene or phenyl chloride, being the analogue of $CH_3.Cl$, monochlor-methane or methyl chloride, or C_2H_5Cl, monochlor-ethane or ethyl chloride.

With toluene and the higher members of the benzene series, however, we have the possibility of the replacement of the hydrogen of the side-group as well as the hydrogen of the nucleus.

giving rise to a great number of isomers. The halogen atoms which are attached to the nucleus are much more firmly held than those which enter in the side-group only. Ammonia and oxidizing agents will attack and eliminate the chlorine of the side-group, but not affect that contained in the nucleus. This action of oxidizing agents is so distinctly different as to serve to distinguish whether the chlorine is present in the one position or the other.

SUMMARY OF HALOID SUBSTITUTION PRODUCTS.

C_6H_5Cl, Chloro-benzene, b. p. 133°.	C_6H_5Br, Bromo-benzene, b. p. 154°.	C_6H_5I, Iodo-benzene, b. p. 185°.
$C_6H_4Cl_2$, Dichloro-benzenes.	$C_6H_4Br_2$, Dibromo-benzenes.	Diiodo-benzenes.
o- 179°, *m*- 172°, *p*- 173°.	*o*- 224°, *m*- 219°, *p*-219°.	

$C_6H_3Cl_3$, Trichloro-benzenes, three isomers.
$C_6H_2Cl_4$, Tetrachloro-benzenes, three isomers.
C_6HCl_5, Pentachloro-benzene.
C_6Cl_6, Hexachloro-benzene, m. p. 226°, b. p. 332°.

$C_6H_4Cl(CH_3)$	Isomeric with	$C_6H_5.CH_2Cl$.
Chloro-toluenes, three isomers.	" "	Benzyl chloride, b. p. 179°
$C_6H_3Cl_2(CH_3)$	" "	$C_6H_5.CHCl_2$.
Dichloro-toluenes, six isomers .	" "	Benzal chloride, b. p. 206°.
——— ———		Benzo-trichloride, b. p. 213°.
——— ———		$C_6H_5.CCl_3$.
$C_6H_3Cl(CH_3)_2$	" "	$C_6H_4(CH_3)CH_2Cl$.
Chloro-xylenes, six isomers .	" "	Xylyl chlorides.

Modes of Formation.—Chlorine and bromine acting upon benzene readily yield monochloro- and monobromo-benzene. A further substitution takes place especially easily in the presence of iodine. This acts as a carrier of chlorine or bromine, and by its presence aids in the introduction of these elements.

In the homologues of benzene, if the chlorination takes place in the cold, the chlorine enters the nucleus; if at a boiling temperature, it enters the side-group.

The action of phosphorus pentachlorides upon phenols and aromatic alcohols also serves to form the halogen derivatives.

The nitro or primary amido compounds of the benzene hydrocarbons may also be converted into halogen compounds by first

converting them into the diazo compounds, and then boiling these with cuprous chloride:

$$C_6H_5.N{=}N.Cl = C_6H_5Cl + N_2.$$

Monochloro-benzene, C_6H_5Cl,
Monobromo-benzene, C_6H_5Br,
Monoiodo-benzene, C_6H_5I,
} are all colorless liquids of peculiar, aromatic odor. The boiling points have been given in the table.

Benzyl Chloride, $C_6H_5.CH_2Cl$, is formed by the action of chlorine upon toluene at a boiling temperature. When oxidized it yields benzoic acid. This reaction, together with the fact that prolonged boiling with water or potassium carbonate solution changes it into benzyl alcohol, $C_6H_5.CH_2OH$, shows that the chlorine is present in the side-group. Colorless liquid, boiling at 179°. It is used on a large scale for the manufacture of benzoic aldehyde (oil of bitter almonds).

Benzal Chloride, $C_6H_5.CHCl_2$, is produced by the further chlorination of boiling toluene, also from benzoic aldehyde by the action of PCl_5.

It is used in the manufacture of benzaldehyde and benzoic acid. When heated with water or sulphuric acid, or, as is done on a large scale, with water and calcium hydrate, the benzal chloride is changed into the aldehyde, $C_6H_5CHCl_2 + H_2O = C_6H_5.CHO + 2HCl$.

Benzo-trichloride, $C_6H_5.CCl_3$, sometimes termed Phenyl-chloroform, is used on a large scale for the manufacture of artificial benzoic acid. For this purpose it is heated with water under pressure:

$$C_6H_5.CCl_3 + 2H_2O = C_6H_5\,COOH + 3HCl.$$

III. Sulphonic Derivatives.

The sulphonic acids of the aromatic series, like those mentioned under the methane derivatives, contain the monad group HSO_3, but are much more readily formed. They result from the action of strong or fuming sulphuric acid upon a great variety of aromatic compounds, and play quite an important part in the technical application of the benzene derivatives, and latterly in the manufacture of synthetic compounds of medicinal value. Thus we may have the following classes of sulphonic acid derivatives:

1. Sulphonic acids of the hydrocarbons, as benzene-sulphonic acid, $C_6H_5HSO_3$.

2. Sulphonic acids of the phenols, as phenol-sulphonic acid, $C_6H_4(OH)HSO_3$.

3. Sulphonic acids of the amines, as amido-benzene-sulphonic acid, $C_6H_4(NH_2)HSO_3$.

4. Sulphonic acids of the diazo compounds, as diazo-benzene-sulphonic acid, $C_6H_4<^{SO_3}_{N:N}>$.

5. Sulphonic acids of the azo compounds, as azo-benzene-sulphonic acid, $C_6H_5.N:N—C_6H_4HSO_3$.

6. Sulphonic acids of the hydrazines, as phenyl-hydrazine-sulphonic acid, $C_6H_5.NH—NH—HSO_3$.

In general, these sulphonic acids and their salts are very stable compounds, mostly soluble in water, difficultly soluble in alcohol.

When fused with caustic potash or soda, they yield phenols and sulphites, $C_6H_5.NaSO_3 + NaOH = C_6H_5.OH + Na_2SO_3$.

When distilled with potassium cyanide, they yield cyanides or nitriles.

When heated with fuming hydrochloric acid or with water under pressure, they regenerate the same hydrocarbons from which they were originally formed, $C_6H_5.HSO_3 + H_2O = C_6H_6 + H_2SO_4$.

Benzene-monosulphonic Acid, $C_6H_5.HSO_3$, is obtained by heating benzene with concentrated sulphuric acid. The excess of sulphuric acid is removed by addition of barium or lead carbonate, as both the barium and lead salts of the sulphonic acid are soluble. It forms small, crystalline leaflets, deliquescing in the air, and easily soluble in water. Because of the fact stated above, that when fused with caustic alkalies it yields phenol, it is of importance in the manufacture of synthetic carbolic acid.

Benzene-disulphonic Acids, $C_6H_4(HSO_3)_2$.—Three isomers are obtainable. The para compound when fused with caustic alkali yields the diatomic phenol, resorcin. (See Resorcin.)

Toluene-sulphonic Acids, $C_6H_4(CH_3)HSO_3$, exist in three isomeric modifications.

Xylene-sulphonic Acids, $C_6H_3(CH_3)_2HSO_3$.—The different isomers of this substance are utilized to separate the isomeric xylenes. (See p. 740.)

The higher homologues of benzene, except hexamethyl-benzene, are all capable of yielding sulphonic acids.

The sulphonic acids of the several classes of benzene derivatives will be mentioned, when of sufficient importance, under the different groups of compounds.

IV. Nitro Derivatives.

By the action of strong nitric acid upon the aromatic hydrocarbons, derivatives in which one or more hydrogen atoms are replaced by the monad group, NO_2, are formed. These are mostly soluble in the strong nitrating acid, and are thrown out of solution on dilution with water. Thus, from benzene we have $C_6H_6 + NO_2.OH = C_6H_5.NO_2 + H_2O$, and from toluene $C_6H_5.CH_3 + NO_2OH = C_6H_4(CH_3)NO_2 + HOH$. When more than one such replacement takes place, we distinguish by the names mononitro-benzene, dinitro-benzene, trinitro-benzene, etc.

In all these cases the NO_2 group attaches itself to the nucleus, and not to the side-group. Whether one or more such replacements shall take place is dependent upon the strength of the acid and the length of time of its action.

The nitro compounds are mostly pale yellowish liquids, distilling undecomposed in a current of steam, or, in the case of the higher derivatives, yellowish needles or prisms. They are heavier than water, and insoluble therein, but generally soluble in alcohol, ether, and glacial acetic acid. All the nitro compounds are reduced in acid solution by the action of nascent hydrogen, forming the corresponding amido compounds. This may be effected by the action of tin and hydrochloric acid, stannous chloride and hydrochloric acid, or iron and acetic acid. Thus, $C_6H_5.NO_2 + H_6 = C_6H_5.NH_2 + 2H_2O$ and $C_6H_4(NO_2)_2 + H_{12} = C_6H_4(NH_2)_2 + 4H_2O$.

The nitro compounds are of very great technical importance as necessary steps in the manufacture of aniline and similar amido compounds.

Nitro-benzene, $C_6H_5.NO_2$, is formed by adding benzene gradually to well-cooled fuming nitric acid as long as it seems to dissolve. After some standing the nitro-benzene is separated by the addition of water, washed with water and dilute caustic soda, and purified by distilling in a current of steam. It forms a light yellowish liquid smelling strongly of bitter almonds, boiling at 205°, and crystallizing in needles at 3°. It is manufactured on a large scale as a step in the manufacture of aniline, and pharmaceutically, under the name of "mirbane oil," as a basis of toilet preparations, soaps, etc., because of its characteristic odor. It is poisonous.

Dinitro-benzenes, $C_6H_4(NO_2)_2$, are formed when benzene is added to a mixture of equal volumes of concentrated nitric and

sulphuric acids and the mixture heated to boiling. All three isomers are solid and crystallizable.

Nitro-toluenes, $C_6H_4(CH_3)NO_2$.—When toluene is acted upon by strong nitric acid, the ortho- and paranitro-toluenes are formed, the meta compound being absent, although obtainable by indirect means. By boiling with fuming nitric acid the nitro-toluenes are changed into dinitro-toluenes.

Commercial benzene, being always a mixture of benzene and toluene, yields on nitration a mixture of nitro-benzene with the several nitro-toluenes above mentioned.

The presence of a halogen atom replacing an atom of hydrogen in the benzene nucleus does not interfere with the nitration, so that compound derivatives are easily formed. Thus, chloro-benzene is readily nitrated, and yields three isomeric chloronitro-benzenes.

A derivative of this character is trinitrochloro-benzene, $C_6H_2(NO_2)_3.Cl$, which acts like an acid chloride, and corresponds to $C_6H_2(NO_2)_3OH$, the so-called "picric acid" (see Trinitro-phenol, or Picric Acid).

V. Amido Derivatives of the Benzene Hydrocarbons.

In studying these compounds it is necessary to remember that they can be looked at from two points of view: first, as benzene in which one or more atoms of hydrogen of the nucleus are replaced by the group NH_2, or as ammonia in which one or more hydrogen atoms are replaced by the radical C_6H_5, or similar aromatic hydrocarbon radical. Thus, $C_6H_5NH_2$ is called amido-benzene when looked at from the first point of view, or phenyl-amine when looked at from the second point of view, and considered as analogous to methylamine, $CH_3.NH_2$. Moreover, just as we had secondary and tertiary amines like dimethylamine and trimethylamine, so we have diphenylamine and triphenylamine. We have, also, the classes of monamines and diamines according as one or two molecules of ammonia are taken as the basis of replacement. The amido group NH_2 can also replace hydrogen of the side-group in the homologues of benzene.

In the accompanying tables we have indicated first the primary amines, which, containing the group NH_2, may also be called amido compounds, and then compared with these the secondary and tertiary amines, containing NH and N respectively, combined with aromatic radicals.

I. TABLE OF PRIMARY AMINES. AROMATIC AMIDO-DERIVATIVES.

From Benzene.	From Toluene.	From Xylene.	From Pseudo-cumene.
$C_6H_5.NH_2$, Aniline, b. p. 183°.	$C_6H_4(CH_3).NH_2$, Toluidines: *o*- b. p. 199°, *m*- 200°, *p*- 198°.	$C_6H_3(CH_3)_2.NH_2$, Xylidines; six isomers.	$C_6H_2(CH_3)_3.NH_2$, Pseudocumidine.
$C_6H_4(NO_2).NH_2$, Nitranilines.	$C_6H_5.(CH_2.NH_2)$, Benzylamine. $C_6H_5.(CH_2.CH_2.NH_2)$, Phenethylamine.		
$C_6H_4(NH_2)_2$, Phenylenediamine.	$C_6H_3(CH_3)(NH_2)_2$, Toluylenediamine.		
$C_6H_3(NH_2)_3$, Triamido-benzene.			

II. TABLE OF SECONDARY AND TERTIARY AMINES.

Secondary.	Tertiary.
$(C_6H_5)_2.NH$, Diphenylamine.	$(C_6H_5)_3N$, Triphenylamine.

Basic Substituted Amines.

$C_6H_5.NH.CH_3$, Methyl-aniline. $C_6H_5.NH.C_2H_5$, Ethyl-aniline. $(C_6H_5)_2N.NO$, Nitrosodiphenyl-amine.	$C_6H_5.N(CH_3)_2$, Dimethyl-aniline. $C_6H_5N(C_2H_5)_2$, Diethyl-aniline. $C_6H_4(NO).N(CH_3)_2$, Nitrosodimethyl-aniline.

Acid Substituted Amines (Anilids).

$C_6H_5.NH(C_2H_3O)$, Acetanilid. $(C_5H_5.NH)_2CO$, Carbanilid. $(C_6H_5NH)(NH_2)CS$, Phenyl-sulphurea.	$C_6H_5.N(CH_3)(C_2H_3O)$, Methyl-acetanilid. $(C_6H_5.N)CO$, Phenyl-cyanate. $(C_6H_5N)CS$, Phenyl mustard oil.

1. **Primary Monamines.**—This most important class are formed most readily by the reduction of the corresponding nitro compounds in acid solution, as already mentioned. This is the process used in the technical manufacture of aniline and its homologues. If a dinitro compound is taken, we may obtain by partial reduction a nitro-amido compound, such as nitraniline. Primary monamines, with the NH_2 groups in the side-chain, like benzylamine, are formed differently. These result from the action of ammonia upon such halogen derivatives as contain the halogen in the side-group: $C_6H_5.CH_2Cl + NH_3 = C_6H_5.CH_2NH_2 + HCl$.

The determination as to whether the amido group may be attached to the nucleus or to the side-group can be had by one of two reactions: first, only those with the amido group in the side-chain result by the action of ammonia upon a haloid derivative of a hydrocarbon; second, only the primary amines with the NH_2 group in the nucleus are changed by nitrous acid into diazo compounds, according to the reaction

$$\underset{\text{Aniline Hydrochlorate.}}{C_6H_5NH_2.HCl} + HNO_2 = \underset{\text{Diazo-benzene Chloride.}}{C_6H_5{-}N{=}N{-}Cl} + 2H_2O.$$

Two other characteristic and important reactions for primary amines may be mentioned. By the action of acids or acid anhydrides upon these amines the hydrogen of the NH_2 group is replaced by an acid radical. These compounds are called anilids:

$$\underset{\text{Aniline.}}{C_6H_5NH_2} + \underset{\text{Acetic Acid.}}{CH_3COOH} = \underset{\text{Acetanilid.}}{C_6H_5NH(CH_3CO)} + H_2O.$$

With chloroform and alcoholic potash solution the primary amines of the benzene series, just as those of the methane series, yield the fearful-smelling carbylamines (isonitriles):

$$C_6H_5NH_2 + CHCl_3 + 3KOH = C_6H_5{-}NC + 3KCl + 3H_2O.$$

Aniline (Amido-benzene or Phenylamine), $C_6H_5.NH_2$, was first obtained in 1826 from the dry distillation of indigo (Portuguese *anil*). It is also contained in coal-tar and in bone-oil. Colorless, oily liquid, turning yellow or brown on exposure to the air. Possesses a weak but peculiar odor. Boils at 184°, and solidifies at —8°. It has no action upon litmus, but is a weak base. It is poisonous, and is a good solvent for many compounds like indigo and sulphur. Unites like ammonia by direct addition to acids to form salts like $C_6H_5.NH_2.HCl$ and $(C_6H_5NH_2)_2.H_2SO_4$.

Small quantities of aniline in solution are recognized by the action of a solution of bleaching powder, which gives a violet color transient in character. A solution of aniline in concentrated sulphuric acid is first colored red and then deep blue by a grain of potassium bichromate. A solution of $K_2Cr_2O_7$, on the other hand, in acid solution of aniline sulphate produces a dark-green color, which in the end gives a precipitate of aniline black. The aqueous solution of aniline sulphate colors paper pulp made from wood-fibre intensely yellow. This is used as a test for wood-pulp in paper.

Substituted Anilines.—The modification of the aniline molecule may arise from the replacement of hydrogen of the nucleus by replacing groups, or by the replacement of the hydrogen in the amido group NH_2.

a. Substituted Anilines with Replacement in the Nucleus.—We may have according to theory three isomeric chloro-, bromo-, or iodo-anilines. These are of no present importance. We may have also three isomeric *Nitranilines*, $C_6H_4(NO_2)NH_2$. These all crystallize in yellow needles or prisms, readily soluble in alcohol, but only slightly soluble in water. They go into the phenylenediamines, $C_6H_4(NH_2)_2$, on reduction. They are also converted into nitrophenols when boiled with alkalies, ammonia being liberated.

Amido-benzene-sulphonic Acids, $C_6H_4(HSO_3).NH_2$.—By heating aniline with fuming sulphuric acid, as well as by the heating of aniline sulphate to 185° to 200°, the para acid, known as *Sulphanilic Acid*, is formed. It crystallizes with one molecule of water in somewhat difficultly soluble rhombic tablets. The meta acid, known as *Metanilic Acid*, finds application, as well as the sulphanilic acid, in the manufacture of azo dye-colors.

b. Substituted Anilines with Basic Groups in Side-Chain.—By the action of aniline chlorhydrate and an alcohol we have formed such compounds as :

Methyl-aniline, $C_6H_5.NH(CH_3)$, which is lighter than water, and has an odor like that of aniline, but stronger and more aromatic.

Dimethyl-aniline, $C_6H_5.N(CH_3)_2$, is an oil of sharp odor, solidifying at 0.5° and boiling at 192.6°. When oxidized with mild oxidizing agents it is changed into methyl violet, one of the aniline dyes. With benzo-trichloride, $C_6H_5.CCl_3$, dimethyl aniline reacts to form malachite green.

c. Substituted Anilines with Acid Groups in Side-Chain.— These are also known as *Anilids*. They are formed by the action of acid anhydrides or acid chlorides upon aniline.

Formanilid, $C_6H_5.NH(HCO)$, is obtained by the rapid distillation of 93 parts of aniline with 126 parts of crystallized or 90 parts of dehydrated oxalic acid: $C_2O_4H_2 + C_6H_5.NH_2 = H_2O + CO_2 + C_6H_5NH(HCO)$.

It forms colorless crystals, melting at 46°, tolerably easily soluble in water, easily soluble in alcohol. Is decomposed by dilute acids. Used for both external and internal use, as a local anæsthetic or as an antipyretic.

Acetanilid, $C_6H_5.NH(C_2H_3O)$ (**Acetanilidum, U.S.P.**).—100 parts of pure aniline and 100 parts of glacial acetic acid are boiled in a round-bottomed flask provided with inverted condenser for from one to two days, until a drop taken out for testing perfectly solidifies on cooling, or until a drop added to dilute caustic soda solution shows no free aniline. It is then fractionally distilled. When the water produced in the reaction has distilled off, the temperature, as shown by the thermometer, rises rapidly, and the Liebig condenser is changed for a straight glass tube, not cooled in any way, as otherwise the acetanilid solidifying in the tube would cause stoppage. The pure substance distils at 295°, and solidifies on cooling. It may be recrystallized out of boiling water. It forms colorless, odorless scales, neutral to test-paper, melting at 112°, and boiling, as said, at 295°. Difficultly soluble in cold water, more readily in hot water, readily in alcohol and ether. Is decomposed by hydrochloric acid into aniline and acetic acid. Heated with dry zinc chloride to 250°–270° it yields "flavaniline," $C_{16}H_{14}N_2$, a dye-stuff, dissolving in hydrochloric acid with moss-green color. First introduced under the name of "antifebrin," and largely used as an antipyretic and antineuralgic. In some cases it has been used for external use as an antiseptic.

Para-bromacetanilid, $C_6H_4BrNH(C_2H_3O)$, has been used in medicine under the name of "antisepsin" or "asepsin."

Methyl-acetanilid (Exalgin), $C_6H_5.N(CH_3)(C_2H_3O)$, is best made by the acetylating of monomethyl-aniline by a method analogous to that described for acetanilid, or by the action of methyl iodide upon sodium-acetanilid. Forms large crystalline needles, difficultly soluble in cold water, easily soluble both in dilute and concentrated alcohol. It fuses at 100°, boils between 240° and 250° without decomposition, and then solidifies in large hair-like crystals. Has been used as an antineuralgic.

Benzanilid, $C_6H_5.NH(C_6H_5CO)$, is formed by the action of benzoic anhydride or benzoyl chloride upon aniline. Colorless, pearly, lustrous scales, distilling without decomposition. Insoluble in water, moderately soluble in cold alcohol, more readily in hot alcohol. Used as an antipyretic.

Gallanilid, $C_6H_5.NH(C_6H_2(OH)_3CO)$. — Made by heating gallic acid with an excess of aniline for an hour to 150°. The pure compound fuses about 205°, and is difficultly soluble in cold water, more readily soluble in hot water, soluble in alcohol and ether. Has been used instead of pyrogallol in skin diseases for external application.

Toluidines, $C_6H_4(CH_3)NH_2$.—The three toluidines are formed by the reduction of the three nitro-toluenes. Para-toluidine, which is solid, and ortho-toluidine, which is liquid, are both present in coal-tar. In manufacturing commercial aniline by the reduction of commercial nitro-benzene, there is always formed a mixture of the two toluidines with aniline, as the original benzene is contaminated with toluene.

Xylidines, $C_6H_3(CH_3)_2NH_2$.—The six possible isomeric xylidines are all known. The technical xylidine contains several isomers, and is largely used for the manufacture of azo dye-stuffs.

Benzylamine, $C_6H_5CH_2.NH_2$, is isomeric with the toluidines. A colorless, basic liquid, boiling undecomposed. Formed most readily by heating benzyl chloride, $C_6H_5.CH_2Cl$, with acetamide, $NH_2(C_2H_3O)$, when the acetyl derivative is formed, from which the base may be obtained.

2. **Secondary Monamines.**—We have, as the first representative of this class :

Diphenylamine, $(C_6H_5)_2.NH$, which is obtained technically by heating aniline chlorhydrate with aniline under pressure :

$$C_6H_5NH_2.HCl + C_6H_5.NH_2 = C_6H_5.NH—C_6H_5 + NH_4Cl.$$

It forms white scales, with an agreeable odor of flowers, and a burning aromatic taste ; hardly soluble in water, easily soluble in alcohol, ether, and petroleum naphtha. A solution of diphenylamine in concentrated sulphuric acid is colored intensely blue by traces of nitric or nitrous acids, and hence is used for this purpose in water analysis.

The hexanitro derivative of diphenylamine, $C_{12}H_5(NO_2)_6N$, acts as a weak acid. Its ammonia salt is a yellow dye-stuff, known as "aurantia." Methyl-aniline and acetanilid and related com-

pounds already considered may also be ranked as secondary monamines.

3. **Tertiary Monamines.**—The only compound to mention here is :

Triphenylamine, $N(C_6H_5)_3$.—It forms large leaflets, melting at 127°.

4. **Diamines and Triamines.**—The diamines may be formed by several reactions, the simplest of which is the reduction of the dinitro compounds. The three isomeric compounds may be distinguished from each other by characteristic reactions ; thus, the meta diamines with nitrous acid give rise to a class of yellowish-brown azo dye-stuffs :

$$\underset{\text{Metaphenylene-diamine.}}{2C_6H_4(NH_2)_2} + HNO_2 = \underset{\text{Bismarck Brown.}}{C_{12}H_{13}N_5} + 2H_2O;$$

and the paradiamines when reduced with H_2S and then oxidized yield violet or blue sulphur-containing dye-stuffs of the methylene-blue class.

Metaphenylene-diamine, $C_6H_4\begin{cases}NH_2\,(1)\\NH_2\,(3)\end{cases}$, forms crystals melting at 63° and boiling at 276°–277° ; difficultly soluble in water, easily in alcohol and ether. As traces of nitrous acid produce the reaction given above with the formation of a yellow dye, it constitutes a very delicate test for nitrous acid.

Paraphenylene-diamine, $C_6H_4\begin{cases}NH_2\,(1)\\NH_2\,(4)\end{cases}$, forms tablets fusing at 140° and boiling at 267°. When oxidized with ferric chloride or manganese oxide and sulphuric acid, quinone, $C_6H_4O_2$, is formed.

Toluylene-diamines, $C_6H_3(CH_3)(NH_2)_2$, and *Xylylene-diamines*, $C_6H_2(CH_3)_2(NH_2)_2$, are also known and used in the manufacture of dye-colors.

Triamido-benzene, $C_6H_3(NH_2)_3$, and *Tetramido-benzene*, $C_6H_2(NH_2)_4$, are representatives of triamines and tetramines respectively.

More special mention of the important dye-colors which are derived from the amines will be found under triphenyl-methane in a later section.

VI. Diazo and Azo Compounds. Hydrazines.

Both the diazo and the azo compounds contain the dyad group —N=N—. In the diazo compounds this group links together a hydrocarbon radical and an acid, in the azo compounds

it links together two hydrocarbon radicals, as $C_6H_5—N=N—Cl$, diazo-benzene chloride, and $C_6H_5—N=N—C_6H_5$, azo-benzene.

1. **Diazo Compounds.**—This class is of very great scientific and technical interest, and its study has led to the discovery of the very numerous group of azo dye-colors, compounds formed by the reaction of the diazo bodies with the phenols and the amines.

To understand these diazo bodies let us compare the action of nitrous acid upon the primary amines of the methane series and the benzene series respectively. The former are converted into alcohols without the formation of intermediate products, according to the reaction :

$$C_2H_5.NH_2 + NOOH = C_2H_5.OH + N_2 + H_2O.$$

The latter can undergo an analogous change, but there result in their case well-characterized intermediate products, these so-called diazo compounds. Thus :

$$\begin{matrix} C_6H_5.N \\ N.O_2H \end{matrix} \begin{matrix} H_2.H \\ \vdots \\ \vdots \end{matrix} NO_3 = \underset{\text{Diazo-benzene Nitrate.}}{C_6H_5.N=N.NO_3} + 2H_2O.$$

This reaction is carried out in the cold, in fact in a carefully-cooled solution. If the solution is warmed, the reaction goes on to the end result indicated with the other class of amines and a phenol is formed :

$$C_6H_5.N=N.NO_3 + H.OH = C_6H_5.OH + N_2 + HNO_3.$$

Just as the salts of the primary monamines when treated with nitrous acid yield the diazo compounds, so when primary diamines are treated with nitrous acid we obtain *tetrazo compounds*, also of great value as dye-stuffs, particularly for cotton dyeing.

Besides the reaction whereby on heating in solution the diazo compounds decompose with the formation of a phenol, we have a second equally important one. When their salts are heated with alcohol they are changed into the corresponding hydrocarbons with liberation of nitrogen :

$$C_6H_5.N=N.Cl + C_2H_5OH = C_6H_6 + N_2 + HCl + C_2H_4O.$$

By means of these two reactions it is possible to change from an amido compound into either a phenol or back to the original hydrocarbon. Hence their great importance in the synthetic work of organic chemistry. The salts of the diazo compounds are mostly colorless crystalline bodies, which are explosive in dry condition and decompose on strong heating of their aqueous solutions.

Diazo-benzene Chloride, $C_6H_5.N{=}N.Cl$. — Stable only in solution.

Diazo-benzene Nitrate, $C_6H_5N{=}N.NO_3$.—Colorless needles, very explosive.

Diazo-benzene Sulphate, $C_6H_5N{=}N.HSO_4$.—Prisms which explode at 160°.

The free *diazo-benzene*, $C_6H_5N{=}N{-}(OH)$, is a heavy oil of yellow color and aromatic odor, which decomposes easily with liberation of nitrogen.

2. Azo Compounds.—While the reduction of nitro compounds in acid solution leads to the aromatic amines, the use of alkaline reducing agents, such as sodium amalgam, zinc-dust and caustic soda, and potash and alcohol, gives rise to intermediate products. The connection of these with the starting-point nitro-benzene and the end product aniline is shown in the following formulas:

$$C_6H_5.NO_2, \quad \begin{matrix} C_6H_5{-}N \\ C_6H_5{-}N \end{matrix}\!\!>O, \quad \begin{matrix} C_6H_5{-}N \\ \| \\ C_6H_5{-}N \end{matrix}, \quad \begin{matrix} C_6H_5{-}NH \\ | \\ C_6H_5{-}NH \end{matrix}, \quad C_6H_5.NH_2.$$

Azoxy-benzene. Azo-benzene. Hydrazo-benzene.

These three intermediate classes are usually grouped together under the general name of azo compounds.

From azo-benzene, $C_6H_5{-}N{=}N{-}C_6H_5$, may be obtained two important classes of colored derivatives, which are of great value under the name of *azo dye-colors*. By the introduction of the amido group in the place of a hydrogen atom we obtain the amido-azo compounds like $C_6H_5.N{=}N.C_6H_4NH_2$, amido-azo-benzene; by the introduction of the hydroxyl group in the place of a hydrogen atom we obtain the oxyazo compounds like $C_6H_5.N{=}N{-}C_6H_4(OH)$, oxyazo-benzene. These are formed respectively, as mentioned on p. 753, by the action of an amine upon the diazo compounds and the action of a phenol upon the same.

Most of these azo dyes are insoluble in water, but all can be converted by the action of strong sulphuric acid into the corresponding sulphonic acids, and both these and their alkaline salts are soluble in water.

The dyes which are derivatives of amidoazo-benzene are termed "Chrysoïdines," and those which are derivatives of oxyazo-benzene are termed "Tropæölines."

3. Hydrazines.—The aromatic hydrazines, like those in the methane series, are derivatives of hydrazine, $NH_2{-}NH_2$, formed by the replacement of the hydrogen atoms by alcohol radicals.

Phenyl-hydrazine, $C_6H_5.NH—NH_2$, the most important of the class of hydrazines, is prepared by the reduction of diazo-benzene chloride :

$$C_6H_5.N=N.Cl + H_4 = C_6H_5.NH—NH_2.HCl.$$

The base itself fuses at 23° to a colorless oil, insoluble in water, soluble in alcohol and ether, which distils undecomposed at 233°. Forms crystallizable salts. Phenyl-hydrazine is a powerful reducing agent, reducing Fehling's solution even in the cold. Its reaction with aceto-acetic ether to form phenyl-methyl-pyrazolon, as the most important step in the manufacture of "antipyrin," has already been mentioned (see Antipyrin, p. 727). Its most general use, however, is as a reagent, as it combines with aldehydes and ketones, and hence with the sugars, to form crystalline compounds known as *hydrazones* and *osazones*. Phenyl-hydrazine itself is poisonous.

Acetyl-phenyl-hydrazid, $C_6H_5.NH—NH(C_2H_3O)$.—This compound was first prepared in an impure state and introduced to medicine under the name of "pyrodine ;" later, when prepared in a pure form, it was known as "hydracetin." It was strongly recommended as an antipyretic and antineuralgic. It forms colorless, lustrous crystals, which are odorless and nearly tasteless, fusing at 128°–129°.

Phenyl-hydrazine-levulinic Acid, $C_6H_5.NH.N=C<^{CH_3}_{CH_2.CH_2.}$-COOH.—This compound is formed by the condensation of levulinic (aceto-propionic) acid (see p. 667) and phenyl-hydrazine, and was introduced to medicine under the name of "antithermin." Forms colorless, lustrous crystals, fusing at 108°, nearly insoluble in cold water and alcohol, more readily soluble in hot water and alcohol. Has been recommended as an antipyretic.

"Agathin" is the name given to a patented preparation of salicylic aldehyde and methyl-phenyl-hydrazine introduced as an antineuralgic. It forms white leaflets with a slight greenish shade, insoluble in water, soluble in alcohol, ether, benzene and petroleum naphtha, fusing at 74°.

VII. Phenols and their Derivatives and Quinones.

The hydroxyl derivatives of the methane series of hydrocarbons were all called alcohols, although the distinction was made of primary, secondary, and tertiary alcohols. In the case of benzene and its homologues, we must distinguish between the

case where the OH group replaces a hydrogen atom of the nucleus and where it replaces a hydrogen atom of the side-group. In the former case the compounds are called *phenols*, and in the latter *aromatic alcohols*. As the latter contain the group $—CH_2.OH$ characteristic of primary alcohols (see p. 624), they can be oxidized to aldehydes and acids, while the former, which are more like tertiary alcohols, cannot be oxidized without entire decomposition of the molecule.

According to the number of the OH groups introduced in place of hydrogen of the nucleus, we have monatomic, diatomic, triatomic, etc., phenols.

TABULAR VIEW OF THE MORE IMPORTANT PHENOLS.

Monatomic.	Diatomic.	Triatomic.
$C_6H_5.OH$, Phenol, m. p. 42°, b. p. 181°.	$C_6H_4(OH)_2$, Dioxybenzenes: *o-* = Pyrocatechin, 104°–245°; *m-* = Resorcin, 118°–280°; *p-* = Hydroquinone, 169°.	$C_6H_3(OH)_3$, Trioxybenzenes: *v-* = Pyrogallol, 115°–210°; *a-* = Oxyhydroquinone, 140.5°; *s-* = Phloroglucin, 217°.
$C_6H_4(CH_3).OH$, Cresols, *o-* 31°–188°, *m-* 3°–201°, *p-* 36°–198°.	$C_6H_3(CH_3).(OH)_2$, Dioxytoluenes: 1 : 3 : 5 = Orcin, 107°–288°; 1 : 3 : 4 = Homopyrocatechin.	$C_6H_2(CH_3)(OH)_3$, Methyl-pyrogallol.
$C_6H_3(CH_3)_2OH$, Xylenols.	$C_6H_2(CH_3)_2(OH)_2$, Xylorcin.	
$C_6H_2(CH_3)_3OH$, Pseudo-cumenols.	$C_6H(CH_3)_3.(OH)_2$, Mesorcin.	
$C_6H(CH_3)_4.OH$, Durenols. Isomeric with these are: $C_6H_3(CH_3)(C_3H_7).OH$, Thymol, Carvacrol.		
	Tetratomic Phenols.	Hexatomic Phenols.
$C_6(CH_3)_5OH$, Pentamethyl-phenol.	$C_6H_2(OH)_4$, Tetraoxybenzene.	$C_6(OH)_6$, Hexaoxybenzene.

The phenols in chemical character stand between the true alcohols and the organic acids. They combine to form mixed ethers, like anisol, $C_6H_5.OCH_3$, or esters, like phenyl-sulphuric acid, $C_6H_5—OSO_3H$. At the same time they have the character

of weak acids, and form salts with the metals, like $C_6H_5.ONa$, sodium-phenol. The acid character is notably increased by the entrance of NO_2 groups, as in trinitro-phenol (picric acid), $C_6H_2(NO_2)_3.OH$.

Phenols are formed by the dry distillation of many organic substances. Thus, phenol and cresol and their homologues are found in coal-tar and in various wood-tars. They are also formed artificially by numerous reactions, among which may be mentioned:

1. By the fusion of the sulpho acids of the aromatic hydrocarbons with caustic potash, $C_6H_5HSO_3 + 2KOH = C_6H_5.OH + K_2SO_3 + H_2O$.

2. By the action of nitrous acid upon the amido compounds and boiling the diazo compounds which first form with water. The two reactions are:

$$(a)\ C_6H_5NH_2HCl + HNO_2 = C_6H_5N{=}N{-}Cl + 2H_2O.$$
$$(b)\ C_6H_5.N{=}N.Cl + H_2O = C_6H_5.OH + N_2 + HCl.$$

3. By the dry distillation of the aromatic phenol-acids (oxyacids) either with or without lime:

$$\underset{\text{Gallic Acid.}}{C_6H_2(OH)_3.COOH} = \underset{\text{Pyrogallol.}}{C_6H_3(OH)_3} + CO_2.$$

Among the most characteristic reactions of the phenols may be mentioned:

1. The formation of the several classes of derivatives already referred to, in which the H of the hydroxyl is replaced,—viz., phenolates, phenol-ethers, and phenol-esters.

2. The formation of substitution compounds in which hydrogen of the nucleus is replaced by chlorine, bromine, nitro, or sulphonic group.

3. The sodium and potassium phenolates unite with CO_2, when heated under pressure, to form salts of oxyacids:

$$\underset{\text{Sodium Phenol.}}{C_6H_5ONa} + CO_2 = \underset{\text{Sodium Salicylate.}}{C_6H_4(OH)COONa}.$$

4. Many phenols give characteristic colors when ferric chloride is added to their neutral solutions. Thus, with ferric chloride phenol and resorcin give a violet color, pyrocatechin a green color, orcin a blue-violet, and pyrogallol a red color.

1. **Monatomic Phenols.**—From benzene but one monatomic phenol is derived.

Phenol, $C_6H_5.OH$ (**Acidum Carbolicum**, U. S. P.), was discovered in 1834 in coal-tar. It is found in the urine of herbivora

and of man (as phenyl-sulphuric acid), in castoreum, in bone oil, and in coal- and wood-tar. It forms colorless, crystalline needles, fusing at 42°, and boiling at 181°. A small percentage of water liquefies the crystals and keeps it in liquid condition. It is soluble in 15 parts of water at ordinary temperatures, easily soluble in hot water, in alcohol, ether, glycerin, fixed oils, potash, and ammonia; has a strong and characteristic odor, burning taste, and caustic action on the skin. It is a strong antiseptic, even in the impure state (**Acidum Carbolicum Crudum, U. S. P.**), when it contains considerable cresols and higher phenols. Ferric chloride colors it even in dilute solution violet. Bromine water causes a white precipitate of tribrom-phenol. It unites with the alkalies and other bases to form the so-called "carbolates," as $C_6H_5.ONa$.

Both chlorine and bromine readily form substitution compounds with phenol, such as *Trichlor-phenol*, $C_6H_2Cl_3.OH$, and *Tribrom-phenol*, $C_6H_2Br_3.OH$. Both of these are distinguished by their antiseptic and healing power, and have been recommended in medicine. The former is a gas of sharp, penetrating odor, and the latter is a white, crystalline solid, melting at 95°. The bismuth compound of tribrom-phenol is also used as an antiseptic dressing under the name of "xeroform."

Nitro Phenols.—Mono- and dinitro-phenols are known, but the only important compound to note is *trinitro-phenol* (or picric acid). This is formed by the action of fuming nitric acid upon many organic substances, such as indigo, silk, leather, wool, etc. It is ordinarily prepared by the nitration of phenol in the presence of strong sulphuric acid. It crystallizes out of water or alcohol in pale-yellow scales, and out of ether in prismatic needles, which have a bitter taste. It melts at 122.5°, and can be sublimed without decomposition, but on rapid heating it is instantly decomposed with slight explosion. It is an important yellow dye. Its salts are beautifully crystallized, but very explosive when heated or struck. The potassium and ammonium salts are used in various explosive mixtures. Picric acid also forms well-crystallized addition compounds with many of the higher hydrocarbons, as naphthalene and anthracene.

Amido Phenols are formed by the reduction of the corresponding nitro phenols. From para-amido-phenol, $C_6H_4(OH)NH_2$, several important derivatives are obtained. The ethyl ethers of the amido-phenols are called "phenetidins." From the para-amido-phenol just mentioned we obtain then para-phenetidin,

$C_6H_4\begin{cases}OC_2H_5\\NH_2\end{cases}$. When this is treated with glacial acetic acid the acetyl group is introduced, and we obtain *acetpara-phenetidin*, $C_6H_4\begin{cases}OC_2H_5\\NH(C_2H_3O)\end{cases}$, which has been brought into medical use under the name of "phenacetin." It forms white, lustrous crystals, without odor and almost without taste, melting at 135°. It is difficultly soluble in cold water, more readily soluble in alcohol. Phenacetin is one of the best known of the newer antipyretics and antineuralgics.

Related to phenacetin are "phenocoll," which is glycocoll-phenetidin, $C_6H_4\begin{cases}OC_2H_5\\NH.COCH_2NH_2\end{cases}$, the commercial preparation being the chlorhydrate, and "methacetin" or para-acetanisidin, $C_6H_4\begin{cases}OCH_3\\NH.C_2H_3O\end{cases}$.

Phenol-sulphonic Acids are formed by the action of concentrated sulphuric acid upon phenol at low temperatures. The ortho-phenol-sulphonic acid is used in 33⅓-per-cent. solution as an antiseptic, under the name of "aseptol" or "sozolic acid." On keeping, it gradually changes into the isomeric para-phenol-sulphonic acid, which change is also readily effected by heating its solutions. The para acid yields well-crystallized salts, two of which are well known in medicine. The sodium salt, $C_6H_4\begin{cases}OH\\SO_3Na\end{cases}+2H_2O$ (**Sodii Sulphocarbolas**, U.S.P.), forms colorless, rhombic prisms, odorless, and with a cooling, saline and slightly bitter taste. The zinc salt, $Zn(C_6H_5SO_4)_2+2H_2O$, which is official in the British Pharmacopœia, forms colorless, tabular efflorescent crystals. By the action of a mixture of potassium iodide and iodate upon the para-phenol-sulphonic acid is obtained the potassium salt of diiodo-para-phenol-sulphonic acid, which, along with other salts of the same acid, has been introduced into medicine under the name of "soziodol" compounds. They are used as antiseptics and substitutes for iodoform for external use.

Anisol (phenyl-methyl ether), $C_6H_5.OCH_3$, and *Phenetol* (phenyl-ethyl ether), $C_6H_5.OC_2H_5$, are obtained by heating phenol and caustic potash with either methyl or ethyl iodide in alcoholic solution. They are liquids of ethereal odor, the former boiling at 152°, and the latter at 172°.

Cresols, $C_6H_4(CH_3)OH$, are the first homologues of phenol. All three of these compounds are present in coal-tar, and are also

contained in the tar from pine and beech wood. Crude carbolic acid always contains a mixture of these, known technically as "cresylic acids." Ortho-cresol is found in the form of its sulphuric ester in the urine of horses; para-cresol is produced by the decay of albumen (tyrosin), and is found in human urine. Its dinitro compound is a golden-yellow dye, which is used as ammonium or potassium salt under the name of "Victoria orange." Meta-cresol is said to be the most powerful antiseptic, exceeding phenol in power, but is much more poisonous. A derivative of this latter is the triiodo-meta-cresol, $C_6HI_3(CH_3)OH$, introduced into medicine under the name of "losophan."

Thymol, U. S. P., is para-propyl-meta-cresol, $C_6H_3.\overset{1}{C}H_3.\overset{3}{O}H.\overset{4}{C}_3H_7$. It is a phenol found naturally occurring in a number of essential oils. It forms large, colorless, translucent crystals, with an aromatic, thyme-like odor and pungent, aromatic taste. It melts at 50°–51°, and boils at 228°–230°. When triturated with equal quantities of camphor, menthol, or chloral hydrate, it liquefies. It is difficultly soluble in water, readily soluble in alcohol, ether, or chloroform. A derivative of thymol is dithymoldiiodide, $C_{20}H_{24}O_2I_2$, which has been introduced into medicine under the name of "aristol." It is a light, chocolate-colored powder, almost without odor or taste, and is used as a substitute for iodoform.

Isomeric with thymol is *carvacrol*, which is para-propyl-ortho-cresol, $C_6H_3.\overset{1}{C}H_3.\overset{2}{O}H.\overset{4}{C}_3H_7$. It is present in oil of *Origanum hirtum*, and may be prepared by heating camphor with iodine.

Xylenols, $C_6H_3(CH_3)_2OH$. — Of the six possible isomers, *m*-xylenol is found in the creosote of beech-wood tar.

2. **Diatomic Phenols.**—These compounds containing two hydroxyl groups are formed by methods analogous to those given for the monatomic phenols, especially by the method of fusion of the sulphonic acids with potash.

Pyrocatechin, $C_6H_4(OH)_2$, is the ortho compound. It was first formed by the dry distillation of catechin (mimosa catechu), whence the name. It is present in small amounts in human urine, and is formed by the dry distillation of wood, by heating cane sugar, cellulose, and starch with water to 200°–280°. It is also formed by the fusion of many resins with potash. It crystallizes in short, rhombic prisms, which can be sublimed, and are readily soluble in water, alcohol, and ether. The aqueous solution is colored green with ferric chloride and then violet by ammonia.

It possesses reducing properties, causing reduction of silver nitrate even in the cold. Its monomethyl-ether, $C_6H_4\begin{cases}OH\\OCH_3\end{cases}$, is *guaiacol*, and its dimethyl-ether, $C_6H_4\begin{cases}OCH_3\\OCH_3\end{cases}$, is *veratrol*. The first of these forms the main constituent of the beech-wood creosote (**Creosotum**, U. S. P.), making up from 60–90 per cent. of the same. The guaiacol is now obtained pure from the creosote, and introduced into medicine in various preparations as a remedy in phthisis. It forms a colorless, somewhat refractive liquid, of strong, aromatic, not unpleasant odor, boils at 200°–202°, and has a sp. gr. 1.117. It is difficultly soluble in water, easily soluble in alcohol and ether.

Resorcin, $C_6H_4(OH)_2$, is the meta compound and is official (**Resorcinum**, U. S. P.). It is obtained on fusing various resins (galbanum, asafœtida, ammoniac, etc.) with potash. Commercially it is obtained by fusing *m*- and *p*-benzene-disulphonic acids with potash. It forms colorless or faintly reddish needles, with a faint, peculiar odor, and a disagreeable, sweetish and pungent taste. It melts at 119° and volatilizes at a higher heat. It is soluble in water, alcohol, and ether, and reduces an aqueous solution of silver nitrate when warmed, and an alkaline solution in the cold. It gives a dark-violet color with ferric chloride solution. Nitrous acid converts it into a nitroso derivative, $C_6H_4O_2(NO)_2$, the iron salt of which is used in cotton-dyeing under the name of "solid-green." Fused with phthalic anhydride it yields fluoresceïn (see phthaleïn dyes), which dissolves in caustic soda with a green fluorescence. Resorcin is used in medicine as an antiseptic, and on a large scale in the manufacture of fluoresceïn and eosin dye-colors.

Hydro-quinone, $C_6H_4(OH)_2$, is the para-dioxy-benzene. It is prepared by the dry distillation of quinic acid, or its oxidation by means of lead dioxide, by the reduction of quinone, $C_6H_4O_2$, and by the decomposition of the glucoside arbutin. Commercially, it is made by oxidizing aniline with chromic acid mixture. It forms small monoclinic plates, fusing at 169°, readily soluble in hot water, alcohol, and ether. It reduces silver nitrate solution on heating, and Fehling's solution even in the cold. Its alkaline solutions are active reducing agents, and are used in photography as the basis of developing solutions. Ferric chloride produces in its aqueous solutions first a blue color, then a yellow, and soon oxidizes it to quinone. It is used somewhat in medicine on account of its antifermentative and antipyretic characters.

Orcin, $C_6H_3(CH_3)(OH)_2$, is a dioxy-toluene. It is found in many lichens (*Rocella tinctoria*, *Lecanora*, etc.). It is formed when aloes are fused with caustic potash, and can be made synthetically from toluene, by fusing *m*-dibrom-toluene with potash at 280°. It crystallizes in colorless prisms, which turn red. The ammoniacal solution absorbs oxygen from the air, and yields *orcein*, $C_7H_7NO_3$, the chief constituent of commercial archil dye. Related to this latter coloring matter is also *litmus*, the well-known blue vegetable color.

Homo-pyrocatechin, $C_6H_3(CH_3)(OH)_2$, is an isomeric dioxy-toluene. Its methyl-ether is *creosol*, $C_6H_3(CH_3)\begin{cases}OH,\\OCH_3,\end{cases}$ one of the chief constituents, along with guaiacol, of the creosote of beech-wood-tar.

Eugenol, the chief constituent of oil of cloves, is the methyl-ether of an unsaturated phenol, $C_6H_3(OH)_2(CH_2.CH{=}CH_2)$.

3. **Triatomic Phenols.**—Of the three isomeric trioxy-benzenes, the most important is *Pyrogallol*, $C_6H_3(OH)_3$ (**Pyrogallol**, U. S. P.). It is obtained generally by the dry distillation of gallic acid: $C_6H_2(OH)_3COOH = C_6H_3(OH)_3 + CO_2$. It forms light, white, shining laminæ, odorless, and with a bitter taste. It becomes darker on exposure to air and light. It is soluble in water, alcohol, and ether. Its solutions, especially when alkaline, absorb oxygen from the air and turn brown in color. Because of this reaction it is used in gas analysis to absorb free oxygen from gaseous mixtures. This reducing power is also recognized with silver, gold, and mercury solutions. It is largely used in photography as a developer because of this power of reduction of silver salts. Pyrogallol also combines with phthalic anhydride to form the dye-color "gallein."

Phloroglucin, $C_6H_3(OH)_3$, an isomeric trioxy-benzene, is produced in the decomposition of phloretin, a glucoside, and by the fusion of a number of resins (such as gamboge, dragon's blood, catechu, and kino) with caustic potash. It is also obtained synthetically by the fusion of benzene-trisulphonic acid with potash. It forms large prisms, which sublime without decomposition, melting at 218°. With ferric chloride it gives a dark-violet coloration. Phloroglucin colors a pine shaving, moistened with hydrochloric acid, red, and is used for the detection of lignin or wood-fibre in paper, etc.

Oxyhydro-quinone, $C_6H_3(OH)_3$, the third isomeric trioxy-benzene, results from the fusion of hydro-quinone with potash.

4. Tetratomic Phenols.—A tetroxy-benzene, $C_6H_2(OH)_4$, has been prepared from succino-succinic ether. It crystallizes in yellow needles, and is stable when pure.

5. Pentatomic Phenols.—As hexahydro derivatives of a pentatomic phenol, $C_6H(OH)_5$, we must include several compounds which at one time were considered to be pentatomic alcohols, or to belong to the carbohydrates.

Quercite, $C_6H(OH)_5.H_6$.—A sweet-tasting crystalline principle extracted from the oak. It forms colorless monoclinic crystals, melting at 235°.

Pinite, $C_6H(OH)_5.H_6$, is found in the exudation of the California pine (*Pinus lambertiana*). It forms colorless crystals, easily soluble in water, and fusing at over 150°.

Inosite (Phaseomannite), $C_6H_{12}O_6 + 2H_2O$, is found in small amount in the muscular tissue, in the heart, lungs, liver, spleen, kidneys, and brain ; the urine also contains inosite after abundant water drinking.

It is also contained in plants, as green beans, peas, lentils, and grape juice. It crystallizes in rhombic plates, which crumble in the air. Soluble in water, insoluble in alcohol, Melts at 210°. It has no reducing power, nor is it fermentable.

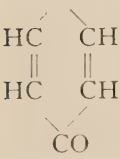
6. Hexatomic Phenols.—We have a derivative of the normal hexaoxy-benzene, $C_6(OH)_6$, in the so-called potassium carbon monoxide, formed in the distillation of metallic potassium, which has the formula $C_6(OK)$. The phenol itself has also been prepared synthetically. It forms small, grayish-white needles, which acquire a reddish color on exposure to the air. They are not fusible, but decompose at about 200°.

Phenose is a hexatomic phenol of hexahydro-benzene, and has the formula $C_6H_6(OH)_6$. It has been obtained by the action of soda solution upon the hypochlorous acid addition product of benzene, $C_6H_6\begin{cases}Cl_3\\(OH)_3\end{cases}$. It is an amorphous, readily soluble, and deliquescent substance. It is much like the glucoses, has a sweet taste, and reduces Fehling's solution, but is not capable of fermentation.

7. Quinones.—This term is applied to a class of benzene derivatives in which two hydrogen atoms seem to be replaced by two oxygen atoms. Not only benzene, but especially the condensed aromatic hydrocarbons, naphthalene, anthracene, phenanthrene, chrysene, etc., when oxidized by chromic acid in glacial acetic acid solution, yield quinones. They are formed also by the oxi-

dation of a number of derivatives of benzene in which the replacing groups occupy the para position. Thus, hydro-quinone (paradioxy-benzene), sulphanilic acid (*p*-amido-benzene-sulphonic acid), and phenylene-diamine, as well as phenol and aniline, all yield quinone when oxidized by chromic acid.

The constitution of quinone, $C_6H_4O_2$, is not definitely settled. By some it is written $C_6H_4\begin{cases}O\\O\end{cases}>$ and by others $C_6H_4<\begin{matrix}O\\O\end{matrix}$ or



According to the first of these formulas quinone would be a peroxide, according to the second a ketone, not of benzene itself, but of a dihydro-benzene. This latter view is now generally accepted, as it brings it into analogy with anthraquinone and the other higher quinones which are known to be diketones.

Quinone (Benzo-quinone), $C_6H_4O_2$, is made most readily by oxidizing aniline sulphate with chromate of potash and sulphuric acid. The quinone so formed is shaken out with ether. Yellow prisms melting at 115.7° and subliming. It has a chlorine-like odor, is difficultly soluble in cold water, more readily soluble in hot water, as well as in alcohol and ether. It is easily converted into hydroquinone by reducing agents like SO_2 or HI.

By chlorinating quinone, or by the action of potassium chlorate and hydrochloric acid upon phenol, we obtain *tetrachlor-quinone* (chloranil), $C_6Cl_4O_2$. As reducing agents convert it readily into tetrachlorhydro-quinone, it is used as an oxidizing agent in the manufacture of aniline colors, as with methyl-violet. Several of the homologues of quinone may also be mentioned, as Toluquinone, $C_6H_3(O_2)(CH_3)$, Xylo-quinone, $C_6H_2(O_2)(CH_3)_2$, and Thymo-quinone, $C_6H_2(O_2)\begin{cases}CH_3\\C_3H_7\end{cases}$.

VIII. Aromatic Alcohols, Aldehydes, and Ketones.

1. Aromatic Alcohols.—The aromatic alcohols differ, as before stated, from the phenols in that the OH has replaced hydrogen in the side-group instead of hydrogen in the nucleus. They may be, and often are, isomeric with phenols, as benzyl alcohol, $C_6H_5.CH_2OH$, and cresol, $C_6H_4(CH_3).OH$.

The comparison of the formula of benzyl alcohol with that of the alcohols of the methane series will make its nature clearer :

$H.CH_2OH$	$CH_3.CH_2OH$	$C_6H_5.CH_2OH.$
Methyl Alcohol.	Ethyl Alcohol.	Benzyl Alcohol.

It is seen here that the single hydrogen of methyl alcohol is replaced by the radical methyl in the second formula, and by the radical phenyl, C_6H_5, in the third formula. Benzyl alcohol is therefore sometimes called phenyl-carbinol

Just as in the methane series of alcohols we have primary, secondary, and tertiary, so we may have primary, secondary, and tertiary aromatic alcohols, as

$C_6H_5.CH_2OH$	Primary alcohol.
$(C_6H_5)_2CH.OH$ and $C_6H_5.CHOH.CH_3$ . . .	Secondary "
$(C_6H_5)_3.C(OH)$	Tertiary "

Diatomic and triatomic alcohols likewise can be formed, as $C_6H_4(CH_2OH)_2$, toluylene alcohols, and $C_9H_9(OH)_3$, phenyl-glycerin.

The strongest analogy of these aromatic alcohols with the corresponding compounds in the methane series is found in the similarity in the effect of oxidizing agents. The primary aromatic alcohols yield aldehydes and monobasic acids, and the secondary yield ketones. Ethers, esters, mercaptans, amines, etc., are also formed in strict analogy to those already studied under the methane series. By the entrance of the phenyl group into unsaturated fatty alcohols we also obtain unsaturated aromatic alcohols analogous to other unsaturated compounds.

Benzyl Alcohol, $C_6H_5.CH_2OH$, is found as benzoic and cinnamic esters in Peru and Tolu balsams, and is made from benzyl chloride, $C_6H_5CH_2Cl$, by boiling it for a time with water, or by the action of potash solution upon its aldehyde, $C_6H_5.COH$:

$$\underset{\text{Benzaldehyde.}}{2C_6H_5.COH} + KOH = \underset{\text{Benzyl Alcohol.}}{C_6H_5.CH_2OH} + \underset{\text{Potassium Benzoate.}}{C_6H_5.COOK.}$$

Benzyl alcohol is a colorless liquid of weak aromatic odor, boiling at 206.5°. It is not very soluble in water. When oxidized it yields first benzaldehyde, $C_6H_5.COH$, and then benzoic acid, $C_6H_5.COOH$.

Tolyl Alcohols, $C_6H_4(CH_3)CH_2OH$.—All three isomeric varieties have been obtained.

Phenyl-methyl Carbinol, $C_6H_5.CHOH.CH_3$, is a secondary alcohol obtained by the action of sodium amalgam upon the cor-

responding ketone, $C_6H_5.CO.CH_3$ (acetophenone), and on careful oxidation reproduces this compound.

Phenyl-propyl Alcohol (Hydrocinnamyl Alcohol), $C_6H_5.CH_2.CH_2.CH_2OH$, is obtained from cinnamyl alcohol by reduction. It exists as cinnamic ester in storax. Closely related to this is the unsaturated aromatic alcohol, known as

Cinnamyl Alcohol (Styrene), $C_6H_5.CH=CH.CH_2OH$.—This occurs as cinnamic ester under the name of styracine in storax resin (**Styrax,** U. S. P.). It crystallizes in shining needles, is sparingly soluble in water, and possesses a hyacinth-like odor. It melts at 33° and distils at 250°. On careful oxidation it yields cinnamic acid; more energetically oxidized it yields benzoic acid.

2. Aromatic Aldehydes.—These correspond in all their general properties with the aldehydes of the methane series.

Benzaldehyde, $C_6H_5.COH$ (**Oleum Amygdalæ Amaræ,** U. S. P.).—This compound was at one time exclusively obtained by the decomposition of the glucoside amygdalin of the bitter almond in the presence of emulsin and other ferments, according to the reaction $C_{20}H_{27}NO_{11} + 2H_2O = C_6H_5.COH + 2C_6H_{12}O_6 + HCN$. It is now mostly made artificially by the oxidation of the chlorine derivatives of toluene:

$$\underset{\text{Benzyl Chloride.}}{2C_6H_5CH_2Cl} + \underset{\text{Benzal Chloride.}}{C_6H_5CHCl_2} + 2MnO_2 = \underset{\text{Benzaldehyde.}}{3C_6H_5.COH} + 2MnCl_2 + H_2O,$$

or by heating benzal chloride with milk of lime under pressure. This reaction has been already noted under benzal chloride (see p. 743).

Benzaldehyde is a colorless, strongly-refracting liquid of pleasant bitter-almond odor. Boils at 179°, and has a sp. gr. of 1.05. It is only slightly soluble in water, but is easily soluble in alcohol and ether. Its behavior shows in many ways its character as an aldehyde. It is easily oxidized to the corresponding acid; it reduces silver solutions with the formation of a metallic mirror; it may be reduced to a primary alcohol; it forms a crystalline compound with sodium bisulphite; it reacts with hydroxylamine and phenyl-hydrazine. A reaction which is distinct and quite characteristic of it as an aromatic aldehyde is its power to unite to form condensation products. Thus, we are able to effect the synthesis of cinnamic acid by the condensation of benzaldehyde and sodium acetate, $C_6H_5.COH + CH_3COONa = C_6H_5CH=CH.COONa + H_2O$, a reaction of the greatest importance in the manufacture of artificial indigo (see Indigo).

Nitro-benzaldehydes, $C_6H_4(NO_2).COH$.—Of these isomers the ortho compound is of especial interest, as by its means artificial indigo has been made, the aldehyde condensing with acetone to form a compound which is decomposed by caustic soda into indigo and acetic acid.

Cumic Aldehyde (Cuminol), $C_6H_4(C_3H_7).COH$.—This is an isopropyl-benzaldehyde. It occurs together with cymene, $C_{10}H_{14}$, in Roman caraway oil and in oil of water hemlock (*Cicuta virosa*). It possesses an aromatic odor, and boils at 235°.

Cinnamic Aldehyde, $C_6H_5.CH=CH.COH$.—This unsaturated aldehyde is the chief constituent of the essential oils of cinnamon and cassia, and can be isolated from them by means of its sodium bisulphite compound. It may also be made synthetically by saturating a mixture of benzaldehyde and acetaldehyde with hydrochloric acid gas, when condensation takes place : $C_6H_5.COH + CH_3.COH = C_6H_5.CH=CH.COH + H_2O$.

It is a colorless, aromatic oil which boils at 247° and distils in a current of steam. When exposed to the air it oxidizes to cinnamic acid.

3. Aromatic Ketones.—The ketones which correspond to secondary aromatic alcohols are in all respects analogous to the corresponding ketones of the methane series. They may be formed by analogous methods : either by the oxidation of the secondary alcohols, or by the distillation of the lime-salts of the aromatic acids.

Aceto-phenone (Phenyl-methyl Ketone, Hypnone), $C_6H_5.CO.CH_3$, is the simplest representative of this class. It is formed by the distillation of a mixture of calcium acetate and benzoate taken in molecular proportions :

$$(C_6H_5.COO)_2Ca + (CH_3.COO)_2Ca = 2CaCO_3 + 2C_6H_5.CO.CH_3.$$

It is a colorless, oily liquid, boiling at 210°, and crystallizing at 14° in large leaflets, which then melt at 20°. It has a peculiar aromatic odor, is difficultly soluble in water, easily soluble in alcohol, ether, chloroform, and fatty oils. When oxidized it yields benzoic acid and carbon dioxide. It has been introduced into medicine as an hypnotic, replacing chloral hydrate and paraldehyde. The name "hypnone" has been given it in this connection.

Phenyl-ethyl Ketone and *Phenyl-propyl Ketone* are also known. The ketone corresponding to benzoic acid, $C_6H_5CO.C_6H_5$, and known as diphenyl ketone, or benzo-phenone, will be mentioned

later under diphenyl-methane. The diatomic and triatomic phenols also react with glacial acetic acid in the presence of zinc chloride to a class of ketones known as keto-phenols.

Gallaceto-phenone, $C_6H_2(OH)_3.COCH_3$, is formed by the reaction between pyrogallol and glacial acetic acid in the presence of zinc chloride. It forms a dirty-flesh-colored, crystalline powder, difficultly soluble in cold water, easily soluble in hot water, alcohol, or ether, and in glycerin. It melts at 170°. It is used in medicine as a substitute for pyrogallol, being relatively non-poisonous, and at the same time strongly antiseptic against micro-organisms.

IX. Phenol Alcohols and Phenol Aldehydes.

1. Phenol Alcohols.—These compounds, as the name indicates, partake of both phenol and aromatic alcohol character; that is, they must contain at least two OH groups, one of which (the phenolic OH) is directly attached to the nucleus, and the other (the alcoholic OH) is contained in the side-group, which will then be CH_2OH. The empirical formulas of the phenol alcohols will always differ by one additional oxygen atom from the aromatic alcohols to which they correspond. Hence they are often called "oxy alcohols."

Oxy-benzyl Alcohols, $C_6H_4(OH)CH_2OH$.—Of the three isomeric compounds of this formula the ortho compound is best known. It is *Saligenin*, which results when the glucoside salicin is decomposed by emulsin or dilute acids: $C_{13}H_{18}O_7 + H_2O = C_6H_4(OH)CH_2OH + C_6H_{12}O_6$.

It forms pearly tablets soluble in hot water, alcohol, and ether, melting at 82°, and subliming near 100°. It yields salicylic acid when oxidized.

Anisyl Alcohol, $C_6H_4(OCH_3)CH_2OH$, is the methyl ether of the *p*-oxybenzyl alcohol, and is obtained from anisic aldehyde by alcoholic potassium hydrate. It crystallizes in needles, melting at 25° and boiling at 259° without decomposition. When oxidized it yields anisic aldehyde and acid.

Vanillin Alcohol, $C_6H_3\begin{cases}OH\\OCH_3\\CH_2OH\end{cases}$, and *Piperonyl Alcohol*, $C_6H_3\begin{cases}O\\O>CH_2\\CH_2OH\end{cases}$, are formed from their aldehydes vanillin and piperonal by acting on their solutions with sodium amalgam.

They are derivatives of the hypothetical protocatechuyl alcohol, $C_6H_3\begin{cases}OH\\OH\\CH_2OH\end{cases}$, as yet unknown. Vanillin alcohol crystallizes in colorless prisms, which melt at 115° and dissolve easily in hot water and alcohol. Piperonyl alcohol forms long prisms melting at 57°, and is difficultly soluble in water.

2. **Phenol Aldehydes** (Oxy Aldehydes).—The phenol aldehydes contain besides the aldehyde group COH the phenolic OH, and show the characters of both aldehydes and phenols, the latter being, however, subordinate. Besides their formation by oxidizing the corresponding alcohols, we have an interesting synthetic method. This consists in the action of chloroform and alkali upon phenols, as: $C_6H_5.OH + CHCl_3 + 4KOH = C_6H_4\begin{cases}OK\\COH\end{cases} + 3KCl + 3H_2O$.

Salicyl Aldehyde, $C_6H_4(OH)COH$.—This is the *ortho-oxybenzaldehyde*. It occurs in the volatile oils of the different varieties of *Spiræa*. It is also obtained by the oxidation of saligenin and salicin, and by the synthetic reaction given above. It is an oil with pleasant aromatic odor, solidifying at 20° and boiling at 196°. It is easily soluble in water, and ferric chloride produces a violet color when added to its solutions. On oxidation it yields salicylic acid. When heated with sodium acetate and acetic anhydride, it undergoes condensation analogous to that mentioned under benzaldehyde, and yields coumarin.

Anisic Aldehyde, $C_6H_4(OCH_3)COH$, is formed in the oxidation of various essential oils (anise, fennel, etc.) with dilute nitric acid or chromic acid mixture. It is a colorless oil, boiling at 248°, with an agreeable odor of flowering hawthorn. On exposure to the air it oxidizes readily to anisic acid, and should therefore be kept in well-stoppered bottles. It is readily soluble in alcohol, and is used in perfumery and in soaps.

Protocatechuic Aldehyde, $C_6H_3(OH)_2COH$.—This compound, the parent substance of vanillin and piperonal, was first obtained from the latter. It may be prepared synthetically from pyrocatechin by the chloroform reaction, or from its ethers, vanillin, isovanillin, and piperonal, by heating them with dilute hydrochloric acid to 200°. It forms crystals soluble in water and melting at 150°. It reduces silver solutions with formation of a mirror. Ferric chloride colors its aqueous solution a deep green.

Vanillin (Methyl-protocatechuic Aldehyde), $C_6H_3\begin{cases}CHO\\OCH_3,\\OH\end{cases}$ is the odoriferous principle of the vanilla bean, which contains from 2 to 2½ per cent., and is found also in many crude beet-sugars, in asparagus, asafœtida, and in small amount in the woody tissue of many plants. It was first made artificially by Tiemann and Haarmann by oxidizing coniferin, a glucoside contained in the cambial juice of the Coniferæ, with chromic acid. It is also formed synthetically together with an isomeric aldehyde (isovanillin) when guaiacol is acted upon with chloroform and alkali, and by oxidizing eugenol from oil of cloves. Vanillin crystallizes in needles, and is soluble in water, alcohol, ether, carbon disulphide, and chloroform. It melts at 80° and boils at 285°. Heated with HCl to 180° it decomposes into methyl chloride and protocatechuic aldehyde. Ferric chloride colors its solution blue.

Piperonal (Heliotropine), $C_6H_3\begin{cases}COH\\O\\O\end{cases}>CH_2$.—This is the methylene ether of protocatechuic aldehyde. It is obtained by oxidizing piperic acid. Forms small, colorless, shining crystals smelling of coumarin, and difficultly soluble in water, but readily soluble in alcohol, ether, vaseline, and glycerin. Melts at 37° and boils at 263°. Is largely used in perfumery as artificial heliotropine.

X. Aromatic Acids and Phenol Acids.

The aromatic acids, like the fatty acids and other acids of the methane series, contain one or more carboxylic groups, COOH, in this case linked either directly or indirectly with the phenyl group or the benzene nucleus. This group COOH, of course, presupposes the side-group CH_3, from which it is formed by oxidation.

TABLE OF AROMATIC ACIDS AND PHENOL ACIDS.

Monobasic Saturated Acids:	Melting Point.
Benzoic acid, $C_6H_5.COOH$	121°
Phenylacetic acid, $C_6H_5.CH_2.COOH$	76°
Toluic acids, $C_6H_4(CH_3).COOH$ — *o*-	102°
Toluic acids, $C_6H_4(CH_3).COOH$ — *m*-	110°
Toluic acids, $C_6H_4(CH_3).COOH$ — *p*-	180°
Hydrocinnamic acid, $C_6H_5.CH_2.CH_2.COOH$	49°
Mesitylenic acid, $C_6H_3(CH_3)_2COOH$	166°
Xylylic acids, $C_6H_3(CH_3)_2COOH$	126°
Xylylic acids, $C_6H_3(CH_3)_2COOH$	163°
Cumic acid, $C_6H_4(C_3H_7)COOH$	116°

TABLE OF AROMATIC ACIDS AND PHENOL ACIDS.—(*Continued.*)

Polybasic Saturated Acids:	
Phthalic acids, $C_6H_4<^{COOH}_{COOH}$	*o*- 213° *m*- 300° *p*- ——
Trimesic acid, $C_6H_3(COOH)_3$	300°
Pyromellitic acid, $C_6H_2(COOH)_4$	264°
Benzene-penta-carboxylic acid, $C_6H(COOH)_5$	——
Mellitic acid, $C_6(COOH)_6$	——
Unsaturated Acids:	
Cinnamic acid, $C_6H_5.CH=CH.COOH$	133°
Atropic acid, $C_6H_5.C<^{CH_2}_{COOH}$	106°
Phenyl-propiolic acid, $C_6H_5.C\equiv C.COOH$	136°
Phenol Acids and Alcohol Acids:	
Salicylic acid, $C_6H_4(OH)COOH$	155°
m- and *p*-oxybenzoic acids, $C_6H_4(OH)COOH$	*m*- 200° *p*- 210°
Anisic acid, $C_6H_4(OCH_3)COOH$	184°
Oxytoluylic acids, $C_6H_3(CH_3)<^{OH}_{COOH}$	——
Melilotic acid, $C_6H_4(OH)CH_2.CH_2.COOH$	128°
Mandelic acid, $C_6H_5.CHOH.COOH$	118°
Tropic acid, $C_6H_5.CH<^{CH_2OH}_{COOH}$	117°
Protocatechuic acid, $C_6H_3(OH)_2COOH$	199°
Vanillic acid, $C_6H_3(OH)(OCH_3).COOH$	207°
Orsellinic acid, $C_6H_2(CH_3)(OH)_2COOH$	176°
Gallic acid, $C_6H_2(OH)_3.COOH$	222°
Tannic acid, $C_{14}H_{10}O_9$	——
Quinic acid, $C_6H.H_6(OH)_4COOH$	162°
Unsaturated Phenol Acid:	
Coumaric acid, $C_6H_4(OH)CH=CH.COOH$	*o*- 208° *p*- 206°

1. **Monobasic Saturated Acids.**—These may be formed by the oxidation of the homologues of benzene, the side-group being changed. Of course the oxidation of the corresponding primary aromatic alcohol may also serve for their formation, as well as the saponification of the cyanides or nitriles of the hydrocarbons (see p. 723). The aromatic acids may undergo in general the same reactions and yield similar classes of products as the fatty acids.

Benzoic Acid, $C_6H_5.COOH$ (**Acidum Benzoicum, U. S. P.**), was discovered in 1608 in gum benzoïn, and prepared from urine by Scheele in 1785. It occurs in the free state in a number of resins and balsams, as gum benzoïn, Peru balsam, Tolu balsam, dragon's blood, and in certain plants. In the urine, especially of carnivorous animals, it occurs as hippuric acid. It is prepared either by sublimation from the gum-resin (*acidum ex resina*), or by the decomposition of hippuric acid (*acidum ex urina*), or synthetically starting from toluene (*acidum ex toluole*). The reaction for this latter production, $C_6H_5CCl_3 + 2H_2O = C_6H_5.COOH + 3HCl$, has already been referred to (see p. 743).

Benzoic acid forms white, lustrous scales, melting at 121°, boiling at 250°, and subliming in a current of steam. The vapors have a peculiar odor, exciting to sneezing and coughing. It is difficultly soluble in cold water, readily soluble in hot water, alcohol, benzene, and petroleum ether.

Of the metallic benzoates we have, as official compounds, **Ammonii Benzoas**, U. S. P., $NH_4C_7H_5O_2$, **Lithii Benzoas**, U. S. P., $LiC_7H_5O_2$, and **Sodii Benzoas**, U. S. P., $NaC_7H_5O_2$. The mercury and bismuth benzoates have also been used in medicine. Both the methyl and the ethyl esters of benzoic acid, $C_6H_5.COOCH_3$ and $C_6H_5.COOC_2H_5$ respectively, are known as pleasant-smelling aromatic liquids, the latter especially, under the name of "benzoic ether," is used in some artificial fruit essences.

Other derivatives of benzoic acid are: benzoyl chloride, $C_6H_5.COCl$, benzonitrile (or phenyl cyanide), $C_6H_5.CN$, benzoic anhydride, $(C_6H_5CO)_2O$, benzamide, $C_6H_5.CONH_2$, and benzanilid, $C_6H_5.CO.NHC_6H_5$. This latter compound is the analogue of acetanilid, and has been introduced into medicine as an antipyretic possessing some advantages over acetanilid.

An important derivative of benzoic acid, and at the same time one of the commercial sources of it, is *hippuric acid* (benzoylglycocoll), $\begin{matrix} CH_2.NH(C_6H_5.CO) \\ | \\ COOH. \end{matrix}$

This compound is obtained from the urine of the herbivora, and in case benzoic acid or compounds capable of yielding it by oxidation are taken internally, from human urine as well. It may be formed artificially by the reaction of benzoyl chloride and glycocoll in the presence of caustic alkali:

$$C_6H_5.COCl + CH_2(NH_2)COOH = C_6H_5CO.NH.CH_2COOH + HCl.$$

It forms rhombic prisms, melting at 187.5° ; difficultly soluble in cold water, easily soluble in hot water and alcohol, but insoluble in petroleum ether and benzene. By boiling with acids or alkalies, as well as by putrefactive decomposition, it is decomposed again into benzoic acid and glycocoll. Of the substituted benzoic acids, such as nitrobenzoic, amidobenzoic, and sulphobenzoic acids and derivatives from them, two compounds may be mentioned : *o*-amidobenzoic acid, known also as *anthranilic acid*, which is obtained when indigo is boiled with caustic potash solution ; and the anhydride of *o*-sulphamid-benzoic acid, which is known commercially as *saccharine*. This compound, although chemically in no way related to the sugars, possesses an extraordinary sweet taste, and is some 280 times sweeter than cane sugar. To prepare it, *o* toluene-sulphonic acid, $C_6H_4(CH_3)SO_3H$, is changed into *o*-toluene-sulphochloride, $C_6H_4(CH_3)SO_2Cl$, and this by the action of ammonia into the sulphamide, $C_6H_4(CH_3)$-SO_2NH_2. This, on oxidation, yields *o*-sulphamid-benzoic acid, $C_6H_4\begin{cases}COOH\\SO_2NH_2\end{cases}$, of which "saccharine" is the anhydride, $C_6H_4\begin{cases}CO\\SO_2\end{cases}>NH$. It forms a white, crystalline powder, fusing at 220° with partial decomposition. It is used for sweetening foods, etc., for diabetic patients where the carbohydrates cannot be allowed. Fused with caustic potash it yields salicylic acid. As this original saccharine is difficultly soluble in water, the sodium salt of the *o*-sulphamid-benzoic acid, $C_6H_4\begin{cases}COONa\\SO_2NH_2\end{cases}$, is also used under the name of "soluble saccharine."

Toluic Acids, $C_6H_4(CH_3)COOH$.—The three toluic acids can be prepared from the three xylenes. Isomeric with them is

Phenyl-acetic Acid, $C_6H_5.CH_2COOH$.—This, as the name indicates, is a phenylated acetic acid. It may be formed synthetically by the saponification of benzyl cyanide, $C_6H_5.CH_2CN$. It forms also in the putrefaction of albuminoids and of wool. It forms scales, melting at 76.5° and boiling at 265.5°.

Xylylic Acids, $C_6H_3(CH_3)_2COOH$.—Of these six are possible and four are known. Isomeric with them are the phenyl-propionic acids, of which there are two : *α-Phenyl-propionic Acid* (Hydratropic Acid), $CH_3—CH(C_6H_5).COOH$, and *β-Phenyl-propionic Acid* (Hydrocinnamic Acid), $CH_2(C_6H_5).CH_2.COOH$. Of these the latter is the more important. It is formed by the action of sodium amalgam upon cinnamic acid, and from the

decay of albuminous matter. It forms fine needles, melting at 47° and boiling at 280°.

Cumic Acid (*p*-Isopropyl-benzoic Acid), $C_6H_4(C_3H_7)COOH$, is obtained by oxidizing Roman oil of cumin with potassium permanganate. It also results from the oxidation of cymene in the animal organism. It crystallizes in plates, and yields cumene when distilled with lime.

2. Polybasic Saturated Acids.—By the oxidation of two or more of the side-groups in the homologues of benzene, polybasic acids are obtained.

Phthalic Acids (Benzene-dicarboxylic Acids), $C_6H_4(COOH)_2$.—We have here three isomers: orthophthalic acid, isophthalic acid, and terephthalic acid. The first is in all respects the most important. It forms when orthoxylene is oxidized by nitric acid or potassium permanganate (not by chromic acid, however, which decomposes it) or any ortho-di-derivative of benzene. It is made on a large scale by the oxidation of naphthalene, either directly with nitric acid or by first forming the tetrachlor-naphthalene, $C_{10}H_8Cl_4$, and then oxidizing this with nitric acid. It crystallizes in short prisms or plates, melting at 184°; readily soluble in water, alcohol, and ether. When heated above its melting point, it readily loses water and yields the anhydride. Distilled with lime it loses CO_2 and yields benzene.

Phthalic Anhydride, $C_6H_4\begin{cases}CO\\CO\end{cases}>O$.—This compound is obtained by sublimation in long, white prisms, melting at 128° and boiling at 284°. When heated with the phenols it yields a series of compounds known as "phthaleïns," such as phenolphthaleïn, resorcinphthaleïn (fluoresceïn), etc. These will be referred to again under Triphenyl-methane and derivatives.

Terephthalic Acid is the para compound. It results from the oxidation of *p*-xylene, cymene, etc., and especially of oil of turpentine or oil of cumin.

Benzene-tricarboxylic Acids, $C_6H_3(COOH)_3$.—Three isomers are known: trimesic acid, obtained by the oxidation of mesitylene; trimellitic acid, obtained by the oxidation of colophony; and hemimellitic acid.

Benzene-tetracarboxylic Acids, $C_6H_2(COOH)_4$.—Of this formula are pyromellitic acid, prehnitic acid, and mellophanic acid.

Benzene-pentacarboxylic Acid, $C_6H(COOH)_5$.—But one acid of this formula is possible and it has been obtained.

Benzene-hexacarboxylic Acid, $C_6(COOH)_6$.—The aluminum

salt of this acid occurs as the mineral mellilite (or honey-stone) in peat and lignite deposits. The acid may also be formed by the oxidation of lignite or graphite with potassium permanganate. It forms fine, silky needles of great stability, easily soluble in water and alcohol. When distilled with lime it yields benzene.

3. Unsaturated Aromatic Acids.—It will be remembered that, besides the saturated aromatic hydrocarbons consisting of benzene and its homologues, we mentioned unsaturated hydrocarbons, such as phenyl-ethylene and phenyl-acetylene (see p. 741). From these are derived alcohols, aldehydes, and acids after the same manner as from the saturated hydrocarbons. Thus, from styrene (phenyl-ethylene), $C_6H_5.CH{=}CH_2$, is derived cinnamyl alcohol, $C_6H_5.CH{=}CH.CH_2OH$, cinnamic aldehyde, $C_6H_5.CH{=}CH.CHO$, and lastly *Cinnamic Acid*, $C_6H_5.CH{=}CH.COOH$. This acid occurs in Peru and Tolu balsams and in storax (both free and as cinnamic esters). It may also be prepared synthetically, as previously mentioned (see p. 766), by the condensation of benzaldehyde and acetic anhydride in the presence of a dehydrating agent like dry sodium acetate :

$$C_6H_5.CHO + H_2CH.COOH = C_6H_5CH{=}CH{-}COOH + H_2O.$$

It crystallizes in prisms, melting at 133° and boiling at 300°–304°. It is difficultly soluble in water, more readily in alcohol, and easily in ether. It can be sublimed, and is volatile in a current of steam. As an unsaturated acid it can add on halogens, haloid acids, and hypochlorous acid. Isomeric with cinnamic acid is

Atropic Acid, $CH_2{=}C{<}\begin{matrix}C_6H_5\\COOH\end{matrix}$. This acid is a decomposition product of the alkaloid atropine, which when boiled with acids or alkalies breaks up into atropic acid, $C_9H_8O_2$, and the base tropine, $C_8H_{15}NO$.

Phenyl-propiolic Acid, $C_6H_5C{\equiv}C.COOH$.—This acid bears the same relation to the unsaturated hydrocarbon phenyl-acetylene that cinnamic acid does to phenyl-ethylene or styrene. It may be formed synthetically by the addition of bromine to ethyl cinnamate, and decomposing the dibromide thus formed with alcoholic potash. Its most important derivative is the *o-nitro-phenyl-propiolic acid*, $C_6H_4(NO_2){-}C{\equiv}C.COOH$, which heated with reducing agents goes over into indigo blue (see Indigo).

4. Phenol Acids.—These compounds are also known as oxy acids, as their empirical formulas show one or more atoms of oxygen in excess of the corresponding aromatic acid. Thus,

benzoic acid is $C_7H_6O_2$, while salicylic (oxybenzoic) acid is $C_7H_6O_3$. In them there is at least one OH group attached directly to the benzene nucleus, and giving to the compound the phenol character, while at the same time they contain the carboxyl group COOH, and act as acids. These phenol acids may form with bases two classes of salts, in one of which the H of the acid group alone is replaced by metal, and in the other of which the H of the phenol group is also replaced. Thus, we have from salicylic acid both $C_6H_4\begin{cases}OH\\COONa\end{cases}$ (neutral sodium salicylate) and $C_6H_4\begin{cases}ONa\\COONa\end{cases}$ (basic sodium salicylate). The first salt is not acted upon by carbonic acid, the second, like the salt of a phenol, is decomposed in aqueous solution by CO_2, and changed into the first compound.

Oxybenzoic Acids, $C_6H_4\begin{cases}OH\\COOH\end{cases}$.—Of the three isomers the most important is the ortho acid, which is **Acidum Salicylicum**, U. S. P. This is found in the blossoms of *Spiræa ulmaria* and as methyl ester in oils of wintergreen and birch. Also obtained by the oxidation of saligenin (see p. 768), and by fusing coumarin, indigo, ortho-cresol, etc., with caustic potash. Synthetically it is now made by the process of Kolbe as improved by Schmidt; acting upon sodium-phenol with CO_2 in closed vessels at a temperature of 130° :

$$C_6H_5ONa + CO_2 = C_6H_5—O—COONa.$$
$$C_6H_5—O—COONa = C_6H_4(OH)COONa.$$

There is formed in this case at first an ether-like compound, sodium-phenol carbonate, and this then by molecular rearrangement passes into sodium salicylate. At a somewhat higher temperature only half the phenol used is converted into salicylic acid, the basic sodium salt is formed, and the other half of the phenol distils off unchanged.

Salicylic acid crystallizes in fine needles, fusing at 158°–159°, and volatile in a current of steam. It is difficultly soluble in cold water, more readily soluble in hot water, easily soluble in chloroform, alcohol, and ether. Ferric chloride produces a violet color in its aqueous solutions.

The salts of salicylic acid which are official are **Lithii Salicylas**, U. S. P., and **Sodii Salicylas**, U. S. P.

Of the esters of salicylic acid, two are official: **Methyl Salicylas**, U. S. P., the artificial or synthetic methyl salicylate, used

in perfumery and in flavoring, and *Phenyl Salicylate* (**Salol**, U. S. P.), which is extensively used in medicine. It is made by the action of salicylic acid upon phenol in the presence of acid chlorides like $POCl_3$ or $COCl_2$. It is a white, crystalline powder, odorless, and almost tasteless. It melts at 42°–43°, and is almost insoluble in water, but soluble in alcohol, ether, chloroform, and fixed or volatile oils. Its alcoholic solution gives a violet color with ferric chloride. It is saponified by caustic soda with liberation of salicylic acid and the odor of free phenol. It is used mainly as an antirheumatic, but also in some cases as an antipyretic and antiseptic.

Both *m-cresol salicylate* and *p-cresol salicylate*, $C_6H_4(OH)$-$COO(C_6H_4CH_3)$, have been proposed as substitutes for salol, liberating the isomeric cresols instead of phenol when saponified.

A substitution derivative of salicylic acid that has been introduced into medicine is *di-iodosalicylic acid*, $C_6H_2I_2(OH)COOH$, prepared by the action of iodine and iodic acid upon salicylic acid in alcoholic solution. It has been used as an analgesic, antipyretic, and antiseptic. The sodium salt of this acid is also used in the same way.

Under the name "salophen" there has also been introduced into medicine acetyl-para-amido-phenol salicylate, $C_6H_4(OH)$-$COO.(C_6H_4NH.COCH_3)$. This compound contains about 51 per cent. of salicylic acid. It is claimed for it that when decomposed in the intestines it yields salicylic acid with antiseptic properties and acetyl-para-amido-phenol with antipyretic properties, and can therefore replace salol to advantage. Both the meta- and the para-oxybenzoic acids are known, the latter being obtained when resins like gum benzoin, dragon's blood, and aloes, as well as tyrosine, are fused with caustic potash.

Anisic Acid, $C_6H_4(OCH_3)COOH$, is the phenol ether of the *p*-oxybenzoic acid. It also results from the oxidation of anisol (see p. 759). It forms rhombic prisms, melting at 184°.

Hydro-cumaric Acids, $C_6H_4(OH).CH_2.CH_2.COOH$.—Of the several isomeric acids of this formula, the ortho-acid, known also as "melilotic acid," occurs in *Melilotus officinalis*, and results from the reduction of coumarin. The para variety, on the other hand, is produced by the decay of tyrosine.

Tyrosine, $C_6H_4(OH).CH_2.CH(NH_2).COOH$. — This amido acid (see p. 657), which crystallizes in fine silky needles, is found in old cheese (*τυρός*), in the pancreatic gland, in diseased liver, in beet-root molasses, etc., and results from albumen, horn, silk,

and similar substances on boiling these with sulphuric acid or from their decay. It is also found in human urine in cases of acute phosphorus poisoning. It has also been made synthetically from phenyl-acetaldehyde.

Isomeric with several of these monobasic phenol acids are several alcohol acids in which we have alcoholic OH in one side-chain and the carboxyl group COOH in another.

Mandelic Acid (Phenyl-glycollic Acid), $C_6H_5.CH(OH).COOH$, results upon heating amygdalin with hydrochloric acid, and is made synthetically by saponifying benzaldehyde cyanhydrin, $C_6H_5.COH.HCN$. Mandelic acid is interesting as entering into the formation of the artificial alkaloid homatropine (see Alkaloids).

Tropic Acid, $C_6H_5.CH\begin{cases}CH_2OH\\COOH\end{cases}$, is formed by the breaking up of atropine and hyoscyamine under the influence of baryta water, the products being tropic acid, $C_9H_{10}O_3$, and tropine, $C_8H_{15}NO$. Tropic acid has also been made synthetically. Prolonged boiling with baryta water changes it into atropic acid (see p. 775).

Protocatechuic Acid, $C_6H_3(OH)_2COOH$, contains two phenol OH groups and the one COOH group. It is obtained by fusing various resins, such as catechu, benzoïn, dragon's blood, asafœtida, and others, with potash. It may be prepared synthetically by heating pyrocatechin with carbonate of ammonia. It forms lustrous needles, melting at 199°, soluble in warm water and alcohol, insoluble in benzene. It reduces ammoniacal silver solution but not Fehling's solution. The solution is colored green by ferric chloride, turning to blue after addition of Na_2CO_3. Putrefactive decomposition changes it into pyrocatechin, $C_6H_4(OH)_2$ and CO_2.

Vanillic Acid, $C_6H_3\begin{Bmatrix}OH\\OCH_3\end{Bmatrix}COOH$, is the monomethyl ether of protocatechuic acid. It results from the oxidation of vanillin or coniferin. Forms needles, melting at 207°, and capable of subliming.

Veratric Acid, $C_6H_3(OCH_3)_2.COOH$, is the dimethyl ether. It occurs in sabadilla seeds (*Veratrum sabadilla*). A homologue of protocatechuic acid is *orsellinic acid*, $C_6H_2(CH_3)(OH)_2COOH$, which is found in many lichens, both free and as an ester, erythrin (see p. 634).

Gallic Acid, $C_6H_2(OH)_3COOH$ (**Acidum Gallicum**, U. S. P.), is found naturally in nutgalls, in tea, in sumac, and in other

plants, and is made synthetically by several reactions. It can readily be prepared from the tannin of nutgalls by the action of dilute acids or by the change due to mould growths. It forms silky needles, fusing at 220° to 240°, and is soluble in hot water, alcohol, and ether. Is decomposed by dry distillation into pyrogallol and carbon dioxide: $C_6H_2(OH)_3COOH = C_6H_3(OH)_3 + CO_2$.

It reduces Fehling's solution, is colored blue-black with ferric chloride, but is not precipitated by lead acetate. With potassium cyanide it gives a red color, and with iodine in the presence of inorganic salts a purplish-red color.

Among the salts of gallic acid may be mentioned the *basic bismuth gallate* (or subgallate), $C_6H_2(OH)_3COOBi(OH)_2$. This compound, discovered in 1841 by Bley, has recently been brought forward as a substitute for iodoform in skin diseases, under the name of "dermatol." It forms a saffron-yellow powder, insoluble in water, alcohol, or ether, but soluble in dilute acids.

Closely related to gallic acid and occurring with it in the several natural sources mentioned is an alteration product of it:

Gallotannic Acid (Digallic Acid), $C_{14}H_{10}O_9$ (**Acidum Tannicum,** U. S. P.).—It is found in gall-nuts to the amount of 60–65 per cent., as well as in sumac, tea, etc. It is best prepared by extracting powdered nutgalls with commercial ether or with acetone. It is a light-yellowish, amorphous powder, or in scales or spongy masses, nearly odorless, and with a strongly astringent taste. It is soluble in water, difficultly soluble in absolute alcohol, and insoluble in absolute ether, benzene, and carbon disulphide. When boiled with dilute acids or alkalies, it takes up a molecule of water and yields 2 molecules of gallic acid. The aqueous solution is colored dark blue by ferric chloride. Tannin has an affinity for the animal hide and for gelatin, and is abstracted from its solution by these substances, the product in the former case being leather.

The salts of tannic acid, or the tannates, are amorphous. The iron salt is the basis of the "nutgall ink," the ferric tannate being kept in suspension by the addition of some gum to the aqueous liquid.

Gallotannic acid is but one of a large series of related tannins which are named according to their sources. The classification adopted by one of the authors in another work * is as follows:

* The Tannins, by Henry Trimble, vol. ii. p. 132, J. B. Lippincott Co., 1894.

Group *a*. Gallotannic acid, Chestnut-wood tannin, Chestnut-bark tannin, Pomegranate-bark tannin, and Sumac tannin.

Group *b*. Oak-bark tannin, Mangrove tannin, Canaigre tannin, Rhatany tannin, Kino tannin, Catechu tannin, Tormentil tannin.

In addition to these, not classified may be mentioned Moritannic acid (from *Morus tinctoria*), Caffe-tannic acid (in coffee), Cinchona tannic acid (in cinchona bark), etc. It has been supposed that a number of these exist in the plants as glucosides, and only show the distinctive characters on the breaking up of this original combination, but all recent investigations indicate that there is no chemical combination of the tannin with glucose.

Quinic Acid, $C_6H.H_6(OH)_4COOH$, is a hexahydro-tetroxybenzoic acid. It is found in quinine bark, in coffee beans, and meadow hay. Forms prismatic crystals, fusing at 161.6°, and soluble in water. When oxidized, yields quinone and hydroquinone, and fused with caustic potash yields protocatechuic acid. The action of reducing agents converts it into benzoic acid :

$$C_7H_{12}O_6 + H_2 = C_7H_6O_2 + 4H_2O.$$

5. Unsaturated Phenol Acids.—These acids, like the unsaturated alcohols and aldehydes, contain an unsaturated side-group with a COOH, and at the same time one or more phenol groups OH.

Coumaric Acid (Oxycinnamic Acid), $C_6H_4(OH).CH=CH.COOH$.—The ortho-coumaric acid is found in sweet clover (*Melilotus officinalis*), and is made synthetically by several reactions, the most interesting of which is the condensation of salicylaldehyde with acetic anhydride in the presence of acetate of soda :

$$C_6H_4(OH)CHO + (CH_3CO)_2O = C_6H_4(OH)CH=CH.COOH + C_2H_4O_2.$$

It forms needles melting at 207°–208°, and subliming when heated. The acid very readily loses a molecule of water and yields the anhydride

Coumarin, $C_6H_4\begin{cases} O \\ CH=CH.CO \end{cases}$. It is found in Tonka beans (the seeds of *Dipterix odorata*), in woodruff (*Asperula odorata*), and other vegetable sources. It may be formed by the synthesis given above for coumaric acid, and in small quantity when malic acid is heated with phenol and sulphuric acid. Forms shining prisms, melting at 67° and boiling at 290°. It is powerfully aromatic, and is employed in perfumery and to impart an aroma to

certain wines. It is scarcely soluble in cold water, but soluble in hot water, alcohol, and ether.

Caffeic Acid (Dioxycinnamic Acid), $C_6H_3(OH)_2CH{=}CH.COOH$, is obtained by the decomposition of the caffe-tannic acid of coffee beans. It may also be formed synthetically by the condensation of protocatechuic aldehyde with acetic anhydride.

Ferulaïc Acid is the methyl derivative of caffeïc acid. It is found in asafœtida, and may be made synthetically from vanillin (methyl-protocatechuic aldehyde) and acetic anhydride.

Umbellic Acid is an isomer of caffeïc acid. Its anhydride is *umbelliferon*, which bears the same relation to this acid that coumarin does to coumaric acid.

Anhydrides of trioxy-cinnamic acids, or, as they may also be termed, dioxy-coumarins, are *Aesculetin* and *Daphnetin*, the products of the decomposition of the glucosides Aesculin and Daphnin.

CHAPTER VII.

AROMATIC COMPOUNDS WITH MORE THAN ONE NUCLEUS.

Two classes are here to be distinguished : compounds in which the several benzene nuclei are joined together without condensation, and compounds in which two or more benzene nuclei have condensed together to form a new and distinctive nucleus or grouping.

I. Compounds with Uncondensed Nuclei.

1. Diphenyl Group.—Just as the action of sodium on methyl iodide in ethereal solution by withdrawing the iodine causes the two methyl groups to unite to form ethane, $CH_3—CH_3$, so the action of sodium on brom-benzene in ethereal solution causes the two phenyl groups to unite to form

Diphenyl, $C_6H_5.C_6H_5$.—It is also formed when the vapor of benzene or benzoic acid is led through a red-hot tube, and is contained in coal-tar. White, lustrous scales, fusing at 71° and boiling at 254°. When oxidized it yields benzoic acid.

The usual replacing groups OH, NO_2, NH_2, HSO_3, and CH_3 may replace hydrogen in the diphenyl formula, and isomeric compounds are formed according to the position of the replacing group.

Among the most important of the diphenyl derivatives may be mentioned

Di-p-amido-diphenyl (Benzidine), $\begin{matrix} C_6H_4.NH_2 \\ | \\ C_6H_4.NH_2 \end{matrix}$. It is obtained by reducing the corresponding nitro compound of diphenyl. It is a diatomic base which crystallizes in colorless, silky plates, readily soluble in hot water and alcohol, and melting at 122°. It is of great importance in the color industry, since its diazo compounds react with phenols and amines to form a valuable class of dyes, which are used on cotton without previous mordanting. These are known collectively as "benzidine dyes."

Carbazole, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!NH$, is the imide of diphenyl. It is con-

tained in coal-tar and in crude anthracene, and may be obtained also by passing diphenylamine (see p. 751) through red-hot tubes.

Hexoxy-diphenyl, $C_{12}H_4(OH)_6$, which dissolves in potash with violet-blue color, is the mother-substance of *Cœrulignone* (or Cedriret), $C_{16}H_{16}O_6$, a violet-colored compound which is formed when crude pyroligneous acid is purified with chromate of potash, and also from the oxidation of the dimethyl-pyrogallol of beech-wood tar. It crystallizes in fine, steel-gray needles, soluble in concentrated sulphuric acid with fine blue color.

2. Diphenyl-methane Group.—The replacement of one hydrogen in methane by phenyl C_6H_5 gives us phenyl-methane, which we have already considered as methyl-benzene, or toluene; the replacement of two or three hydrogen atoms by phenyl groups gives us diphenyl-methane and triphenyl-methane compounds, which, therefore, bear a simple relation to toluene. Thus, we have

$C\begin{cases} H \\ H \\ H \\ H \end{cases}$, Methane. $C\begin{cases} C_6H_5 \\ H \\ H \\ H \end{cases}$, Phenyl-methane, or toluene. $C\begin{cases} C_6H_5 \\ C_6H_5 \\ H \\ H \end{cases}$, Diphenyl-methane. $C\begin{cases} C_6H_5 \\ C_6H_5 \\ C_6H_5 \\ H \end{cases}$. Triphenyl-methane.

Diphenyl-methane, $C_6H_5.CH_2.C_6H_5$, is obtained by the action of benzyl chloride upon benzene in the presence of aluminum chloride or zinc-dust. It forms long, colorless needles, which smell of oranges. Fusing point 26°–27°.

Benzophenone (Diphenyl-ketone), $C_6H_5.CO.C_6H_5$, may be obtained by oxidizing diphenyl-methane with chromic acid, or more simply by distilling benzoic acid with lime. This reaction shows it to be the counterpart of acetone obtained by distilling acetate of lime. Colorless crystals, insoluble in water, soluble in alcohol. It is dimorphous and may crystallize in rhombic prisms, fusing at 49°, or in rhombohedra, fusing at 27°.

Fluorene (Diphenylene-methane), $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!CH_2$, is contained in coal-tar, and crystallizes in colorless plates with a violet fluorescence. It melts at 113° and boils at 295°.

3. Triphenyl-methane Group.—Triphenyl-methane, $CH(C_6H_5)_3$, and its homologues, diphenyl-tolyl-methane, $CH\begin{cases} C_6H_5 \\ C_6H_5 \\ C_6H_4.CH_3 \end{cases}$, and phenyl-ditolyl-methane, $CH\begin{cases} C_6H_5 \\ C_6H_4.CH_3, \\ C_6H_4.CH_3 \end{cases}$

are of especial importance as being the mother-substances of the great majority of the so-called "aniline dyes."

Triphenyl-methane can be made synthetically by a variety of reactions. Thus, by the action of benzal chloride on benzene in the presence of Al_2Cl_6 we have

$$C_6H_5.CHCl_2 + 2C_6H_6 = CH(C_6H_5)_3 + 3HCl,$$

or from chloroform and benzene in the presence of aluminum chloride

$$CHCl_3 + 3C_6H_6 = CH(C_6H_5)_3 + 3HCl.$$

It forms white, prismatic crystals, soluble in hot alcohol and ether, fusing at 92.5° and boiling at 359°.

Triphenyl-carbinol, $(C_6H_5)_3.C(OH)$, may be prepared by oxidizing triphenyl-methane with chromic acid.

Fuming nitric acid acting upon triphenyl-methane produces *trinitro-triphenyl-methane*, $(C_6H_4.NO_2)_3CH$, and this oxidized gives *trinitro-triphenyl-carbinol*, $(C_6H_4NO_2)_3.C(OH)$. The corresponding amido compounds $(C_6H_4NH_2)_3CH$ and $(C_6H_4NH_2)_3C(OH)$ are known as "para-leucaniline" and "para-rosaniline" respectively, and are the starting-points of the aniline-color manufacture.

TRIPHENYL-METHANE DYE-COLORS.

From triphenyl-methane may be derived the four groups of dye-colors which follow, and these, which, in distinction from the nitro dye-colors, the azo dye-colors, or the naphthalene and anthracene dye-colors, are called the triphenyl-methane colors, are the "aniline colors" in the narrower sense of the word. These groups are:

(*a*) The Malachite Green group (Diamido derivatives of Triphenyl methane).

(*b*) The Rosaniline group (Triamido derivatives of Triphenyl-methane).

(*c*) The Rosolic Acid group (Oxy derivatives of Triphenyl-methane).

(*d*) The Phthaleïn group (derivatives of Triphenyl-methane-carboxylic acid).

Phenol-phthaleïn forms colorless needles, fusing at 250°–253°, which are insoluble in water, soluble in alcohol. Alkalies also dissolve it with red color, which the slightest excess of acid causes to disappear. Hence used as an indicator in alkalimetry. (**Phenol-phthaleïn Test-solution, U. S. P.**)

4. The Indigo Group.—In the Indigo plant (*Indigofera tinctoria*), as well as in woad (*Isatis tinctoria*) and other plants, is present a glucoside, *Indican*, which by its decomposition, which takes place by a spontaneous fermentation when the plant is cut,

yields "Indigo blue" along with a sugar-like substance known as "indiglucin."

Indigo (Indigotin or Indigo Blue), $C_{16}H_{10}N_2O_2$, has now been made synthetically by a variety of methods, and its molecular constitution is clearly understood. Its formula is

$C_6H_4<\overset{CO}{NH}>C=C<\overset{CO}{NH}>C_6H_4$. Its synthesis from *o*-nitrophenyl-propiolic acid (see p. 775) has already been referred to, the reaction in this case being $2C_6H_4(NO_2).C\equiv C.COOH + 4H = C_{16}H_{10}N_2O_2 + 2CO_2 + 2H_2O$, the reducing agent in this case being either grape-sugar in alkaline solution or an alkaline xanthogenate.

A second synthesis is effected by the action of dilute alkalies upon a solution of *o*-nitrobenzaldehyde in acetone, the reaction being

$$2C_6H_4(NO_2)CHO + 2C_3H_6O = C_{16}H_{10}N_2O_2 + 2C_2H_4O_2 + 2H_2O.$$

A still later synthesis of different character consists in fusing together phenyl-glycocoll with caustic potash out of access of air, when "indigo white" is formed, which by oxidation at once changes into indigo blue.

$$(a)\ C_6H_5NH.CH_2.COOH = C_6H_4<\overset{CO}{NH}>CH_2 + H_2O.$$

$$(b)\ 2C_6H_4<\overset{CO}{NH}>CH_2 + O_2 = C_6H_4<\overset{CO}{NH}>C=C<\overset{CO}{NH}>C_6H_4 + 2H_2O.$$

Indigo can be obtained from solution in aniline in blue crystals with a coppery-red lustre. It is insoluble in water, alcohol, and ether, but soluble in hot aniline, chloroform, petroleum naphtha, fusel oil, and nitrobenzene. It dissolves in cold sulphuric acid without change, but on heating, the indigo-sulphonic acids are formed. Oxidizing agents like fusing alkalies change it into salicylic and anthranilic acids. Reducing agents change it into indigo white. Indigo has been used from the earliest times for dyeing purposes, being brought from the East Indies.

Indigo White, $C_{16}H_{12}N_2O_2$, results from the reduction of indigo blue.

Sulphonic Acids of Indigo.—Indigo, when treated with fuming sulphuric acid, is converted into a mixture of Indigo-monosulphonic and Indigo-disulphonic Acids, $C_{16}H_9(SO_3H)N_2O_2$ and $C_{16}H_8(SO_3H)_2N_2O_2$ respectively. When the strong acid solution is diluted with water, the first of these is precipitated, insoluble in dilute acids, although soluble in pure water. The second remains

dissolved in the dilute acid solution. Its sodium salt comes into commerce as "Indigo-carmine," or soluble indigo-color.

Isatin, $C_8H_5NO_2$ $\left(\text{or } C_6H_4\begin{matrix}CO\\N\end{matrix}\!\!>\!C(OH)\right)$, is formed by the oxidation of indigo with nitric acid. It forms yellowish-red prisms, soluble in hot water and alcohol, fusing at 200°–201°. When dissolved in excess of concentrated sulphuric acid, it gives a blue color with thiophene, or benzene containing thiophene (see Thiophene, p. 726).

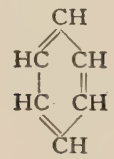
By reduction of isatin are obtained *dioxindol*, *oxindol*, and *indol*.

Indoxyl, $C_8H_7NO\left(\text{or } C_6H_4\begin{matrix}C(OH)\\NH\end{matrix}\!\!>\!CH\right)$, is found in the form of its sulphonic acid in normal urine in small amount and under pathological conditions (stoppage of the intestine) in larger amount. Yields indigo when oxidized. Indoxyl may be tested for in the urine by adding strong hydrochloric acid and a few drops of chlorinated soda as an oxidizing agent, when the blue color of indigo will be obtained.

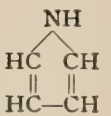
The underlying substance of the whole indigo group is

Indol, $C_6H_4\begin{matrix}CH\\NH\end{matrix}\!\!>\!CH$.—This substance is obtained readily from albuminoids by the action of bacteria, by the pancreatic fermentation, and by fusion with caustic potash. It has also been made synthetically by heating *o*-nitrocinnamic acid with potash and iron filings, by heating aniline with monochloracetaldehyde, and by other reactions. It forms lustrous white leaflets, melting at 52° and readily volatile with steam. It has the peculiar odor of fæces.

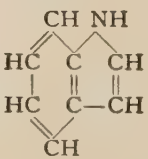
Indol can be considered as the condensation product of a benzene nucleus and a pyrrol nucleus, as illustrated by the structural formulas:



Benzene.



Pyrrol.



Indol.

In this formula, two carbon atoms are common to both the benzene and the pyrrol nuclei. We shall have examples of similar condensation of two or more benzene nuclei in the formulas of naphthalene and anthracene.

Skatol (β-methylindol), $C_6H_4<\begin{matrix}C(CH_3)\\NH\end{matrix}>CH$, is found in the fæces, and is formed from albumen by fusion with potash or by the action of bacteria, generally accompanied by indol. It may also be made synthetically from propionaldehyde and phenylhydrazine. It forms white, lustrous leaflets, melting at 95° and boiling at 265°–266°, and possessing a strong odor of fæces. A pine chip, moistened with an alcoholic skatol solution and then dipped in cold, strong hydrochloric acid, is colored first cherry-red and then dark violet.

II. Compounds with Two Condensed Benzene Nuclei

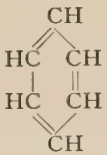
In the higher-boiling portions of coal-tar occur hydrocarbons still richer relatively in carbon than benzene,—that is, containing relatively less hydrogen for a given number of carbon atoms. While the general formula of benzene and its homologues was C_nH_{2n-6}, these hydrocarbons belong mainly in two series, possessing the general formulas C_nH_{2n-12} and C_nH_{2n-18} respectively. These hydrocarbons not only belong to the closed-chain or cyclic hydrocarbons, but they bear a close relationship to benzene, and are, in fact, derivatives of it. This is seen, for instance, in the fact that naphthalene, the representative of the formula C_nH_{2n-12}, when oxidized yields phthalic acid, and anthracene, the representative of the formula C_nH_{2n-18}, when oxidized yields benzoic acid.

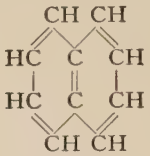
1. **Naphthalene Series.** (General formula C_nH_{2n-12}.)

Naphthalene, $C_{10}H_8$ (**Naphtalinum,** U. S. P.), is a product of destructive distillation of many organic compounds, being formed when ethylene, acetylene, alcohol, ether, acetic acid, camphor, etc., are decomposed by heat, as in passing through a red-hot tube. Is mainly extracted from coal-tar, of which it is an abundant constituent. It forms white, lustrous scales, melting at 79.2° and boiling at 218°, but volatile in a current of steam. Is insoluble in water, soluble in hot alcohol and in ether. Naphthalene has a strong and characteristic coal-tar odor. It is used as an antiseptic and disinfectant, and as a substitute for camphor as a preservative against moths (hence the designation "coal-tar camphor"), and on a large scale for the manufacture of phthalic acid and numerous derivatives used in the dye-color industry, and for carburetting illuminating gas.

The constitution of naphthalene has been established by a study

of its decompositions and is illustrated by the following graphic formulas:

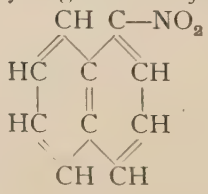

Benzene.

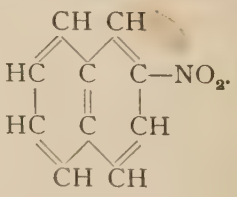

Naphthalene.

In this formula, two benzene nuclei are considered to have condensed, two atoms of carbon being held in common by the two parts which have united. This gives us 10 atoms of carbon, of which only 8, however, are free to attach hydrogen, hence the formula $C_{10}H_8$.

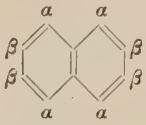
2. Addition Compounds of Naphthalene.—Naphthalene takes up hydrogen far more readily than benzene does, and forms first *naphthalene dihydride*, $C_{10}H_8.H_2$, and *naphthalene tetrahydride*, $C_{10}H_8.H_4$. By more intense action of hydriodic acid and phosphorus the second benzene nucleus is also attacked, and a *hexahydride*, $C_{10}H_8.H_8$, and finally a *dekahydride*, $C_{10}H_8.H_{10}$, are formed. It also yields chlorine addition products more readily than benzene does, such as *naphthalene dichloride*, $C_{10}H_8.Cl_2$, and *naphthalene tetrachloride*, $C_{10}H_8.Cl_4$. This latter is manufactured on a large scale by the action of potassium chlorate and hydrochloric acid upon naphthalene, and is then oxidized by the aid of nitric acid, yielding phthalic acid as product (see p. 774).

3. Substitution Derivatives of Naphthalene.—In speaking of benzene it was stated (see p. 733) that in the case of monosubstitution compounds it mattered not which H atom of the benzene molecule was considered to have been replaced. In the case of naphthalene we find that there are two mono-chlornaphthalenes, two mono-nitronaphthalenes, etc. The reason of this is apparent on examining the structural formula of naphthalene. It will be seen that in the accompanying two cases represented the replacement in the one formula is of a hydrogen attached to a carbon adjacent to one of the two linking carbons, and in the other formula is of a hydrogen not adjacent to either of these linking carbon atoms:





The first of these compounds is called α-nitronaphthalene and the second β-nitronaphthalene.

There are four positions the replacing group may take in the case of the α derivative, and four positions in the case of the β derivative. Thus, in the formula  we have represented the several cases for both α derivatives and β derivatives.

The halogen derivatives of naphthalene possess only slight interest. The α- and β-nitronaphthalenes are chiefly important as furnishing by their reduction the corresponding naphthylamines. These are the counterpart of aniline and its homologues in the benzene series. They find a large application in the manufacture of azo dye-colors.

Both naphthylamines are reducible by sodium in alcoholic solution to tetrahydro-addition compounds. The second of these, tetrahydro-β-naphthylamine, has been introduced into medicine under the name of "thermin." It is a clear, colorless liquid of a piperidine-like odor, and of so energetic basic properties that it forms a stable salt with carbonic acid. It has a mydriatic action, and at the same time raises the temperature of the body quite appreciably. The salt used is the hydrochlorate.

The two naphthalene-monosulphonic acids are also important, both for the manufacture of dye-colors and because by their fusion with caustic alkali they yield the two naphthols.

The naphthols, $C_{10}H_7.OH$, are the simple hydroxyl derivatives —or, in other words, are the phenols—of the naphthalene series. Both are found in coal-tar. *α-naphthol* may be obtained from α-naphthylamine by means of the diazo compound or upon fusing α-naphthalene-sulphonic acid with alkalies. Both reactions are analogous to those used for the preparation of phenol (see p. 757). It is soluble with difficulty in hot water, readily in alcohol and ether, crystallizes in shining needles, and has the odor of phenol. It melts at 95° and boils at 278°–280°.

A nitro derivative of α-naphthol that has been used largely in the dyeing industry is *dinitro-α-naphthol*, $C_{10}H_5(NO_2)_2.OH$. The sodium and calcium salts have been known as "Martius' yellow" (naphthalene yellow). They are, however, difficultly soluble, and have been replaced by the corresponding sulphonate, $C_{10}H_4(NO_2)_2\begin{cases} OK \\ SO_3K \end{cases}$, which is known as "naphthol yellow."

β-Naphthol (**Naphtol,** U. S. P.).—Fuming sulphuric acid acting upon naphthalene at 80°–90° produces *α*-naphthalene-sulphonic acid chiefly, but at 200° *β*-naphthalene-sulphonic acid is the chief product. The sodium salt of this acid is fused with caustic soda, and the result is *β*-naphthol-sodium. From this the official compound is liberated by the addition of hydrochloric acid. It forms colorless, silky scales or crystalline powder of a weak phenol-like odor and sharp taste. It fuses at 123° and boils at 286°. Alkalies produce a bluish-violet fluorescence; ferric chloride produces a greenish color. *β*-naphthol is soluble in alcohol, ether, benzene, chloroform, oils, and alkalies.

It is quite analogous in chemical properties to phenol or carbolic acid. It is largely used for external application as an antiseptic; taken internally it is a poison. *β*-naphthol should be free from contamination with *α*-naphthol, as this is quite poisonous. The ferric chloride test above mentioned serves to distinguish them; with *α*-naphthol a violet color is obtained.

Two derivatives of *β*-naphthol have been introduced into medicine:

β-Naphthyl-salicylate (Betol), $C_6H_4(OH)COOC_{10}H_7$.—This compound is the counterpart of salol, which is phenyl salicylate. It forms a pure white powder of lustrous crystals, melting at 95°. It is difficultly soluble in both cold and hot water, easily soluble in boiling alcohol, ether, benzene, and warm linseed oil. Its therapeutic action is almost the same as that of salol, decomposing in the intestine into salicyclic acid and *β*-naphthol. The other derivative is

β-Naphthol-α-monosulphonate of Calcium (Asaprol).—It has been recommended for internal administration in cases of rheumatism, gout, etc.

Dioxynaphthalenes, $C_{10}H_6(OH)_2$, the counterparts of the diatomic phenols, are also known. Similarly corresponding to quinone, $C_6H_4O_2$, are the *α*- and *β-naphthoquinones*, $C_{10}H_6O_2$. These are produced directly by the oxidation of naphthalene with chromic acid.

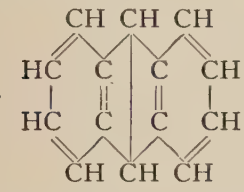
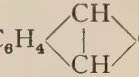
Both the hydroxyl group, OH, and the quinone group, O_2, may exist in the same molecule. We have an *oxynaphthoquinone*, $C_{10}H_5(OH)O_2$, and a *dioxynaphthoquinone*, $C_{10}H_4(OH)_2O_2$. This latter is known as "naphthazarine" (or alizarine black), a valuable dye-color.

Homologues of naphthalene, such as *α*- and *β-methyl-naphthalenes*, are found in coal-tar. From these are derived the *naphthoic*

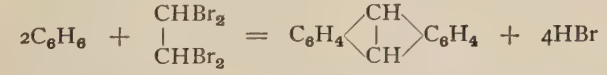
acids, $C_{10}H_7.COOH$, just as benzoic acid is derived from toluene or methyl-benzene, and corresponding to the oxybenzoic acids (such as salicylic acid) we have *α-* and *β-oxynaphthoic acids*. Of these the former has been used in medicine as an antiseptic of very similar character to salicylic acid.

III. Compounds with Three Condensed Nuclei.

Under the general formula C_nH_{2n-18} we have two hydrocarbons of the composition $C_{14}H_{10}$, besides homologues of these. These hydrocarbons are anthracene and phenanthrene, and both occur in coal-tar

1. Anthracene and its Derivatives.—Anthracene is a product of destructive distillation of organic material, such as coal-tar, petroleum, turpentine oil, etc., and can be made synthetically from a variety of sources. Its structural formula is considered to be  , in which formula we have two benzene residues C_6H_4 united by the group C_2H_2 as the middle nucleus. This group, C_2H_2, with the equivalence four, links together the two parts in the manner expressed by the full structural formula given above, or sometimes expressed  .

That the two CH groups which join together the two benzene nuclei are also linked with each other by a single bond is indicated by several reactions, among which may be mentioned the formation of anthracene from benzene and tetrabromethane in the presence of aluminum chloride:



It is obtained from the fraction of the coal-tar boiling above 300° and known as the "green oil" (or anthracene oil) by chilling this and pressing out the crude anthracene in cakes of greenish-yellow color. The pure hydrocarbon forms colorless plates of white color with blue fluorescence. It fuses at 213° and boils above 360°. With picric acid it forms an addition compound, crystallizing in beautiful red needles. It is difficultly soluble in

alcohol and ether, readily soluble in hot benzene or toluene. When oxidized it yields *anthraquinone*, while reducing agents change it to *anthracenehydride*, $C_6H_4<\overset{CH_2}{CH_2}>C_6H_4$, and on prolonged action to *anthracene hexahydride*, $C_{14}H_{16}$, and ultimately to *anthracene perhydride*, $C_{14}H_{24}$.

The chief uses of anthracene are in the preparation of alizarine and similar artificial dye-colors.

Anthraquinone, $C_6H_4<\overset{CO}{CO}>C_6H_4$, is readily obtained by the oxidation of anthracene by chromic acid in glacial acetic acid and by the distillation of calcium benzoate:

$$(C_6H_5.COO)_2Ca = C_6H_4<\overset{CO}{CO}>C_6H_4 + CaO + H_2O.$$

It forms yellow prisms, soluble in hot benzene or glacial acetic acid, fusing at 277°, and boiling at over 360°. By distillation in contact with zinc-dust it yields anthracene again. Fused at high temperatures with caustic potash it yields benzoic acid. By heating with strong sulphuric acid it is made to yield sulphonic acids, such as *anthraquinone-monosulphonic acid*, $C_6H_4<\overset{CO}{CO}>C_6H_3(HSO_3)$, and *anthraquinone-disulphonic acids*, $C_{14}H_6(HSO_3)_2O_2$. These sulphonic acids are of great technical importance as being steps in the synthetic formation of alizarine.

Oxyanthraquinones are formed when hydrogen of the anthraquinone formula is replaced by OH groups. Thus, *mono-oxyanthraquinone* is $C_{14}H_7(OH)O_2$, and *dioxyanthraquinone* is $C_{14}H_6(OH)_2O_2$. Of this latter there are a number of isomers, of which the most important is alizarine. *Trioxyanthraquinones*, $C_{14}H_5(OH)_3O_2$, are also obtained, of which anthragallol and purpurine are the most important. The methods for the formation of these very important technical compounds will be noted later.

Alizarine (Ortho-dioxyanthraquinone), $C_6H_4<\overset{CO}{CO}>C_6H_2(OH)_2$, is found in madder-root (*Rubia tinctorum*), where it results from the decomposition of a glucoside, rubianic acid (ruberythric acid). It has been known from early historic times, and was used in the East for the cotton and damask dyeing known as "Turkey red."

Since 1867, when Graebe and Liebermann first effected its synthesis from anthracene, it has been made artificially in a variety of ways. Thus, the

first synthesis was from anthracene, by the action of bromine upon the anthraquinone, and then fusing the dibromanthraquinone with caustic potash, as shown:

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_4 + 4Br = C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_2Br_2 + 2HBr.$$

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_2Br_2 + 2KOH = C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_2(OH)_2 + 2KBr.$$

This first synthesis was soon superseded by that involving the use of fuming sulphuric acid. The mono- and disulphonic acids when fused with caustic alkali should yield by theory the corresponding oxyanthraquinones. It is found, however, in practice, that oxygen is always absorbed from the air, and that the monosulphonic acid when fused yields a mixture of mono- and di-oxyanthraquinones, and the disulphonic acid yields a mixture of di- and tri-oxyanthraquinones. Chlorate of potash is, therefore, added in practice to facilitate their partial oxidation and to complete the change. The reactions then for the manufacture of alizarine are:

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_3(HSO_3) + NaOH = C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_3(OH) + NaHSO_3.$$

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_3(OH) + O = C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_2(OH)_2.$$

Of course as an excess of the fused alkali is present, the alizarine, as formed, becomes sodium alizarate, $C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_2(ONa)_2$, which is soluble in water with rich purple color. From this solution, on addition of hydrochloric acid, the alizarine is precipitated as a tawny-yellow powder, which generally comes into commerce in the moist state as a 10-per-cent. or 20-per-cent. paste.

Alizarine crystallizes in fine red prisms or needles, which melt at 282°, and can be sublimed. It is readily soluble in alcohol and ether, combines with a violet or purple color with alkalies, and forms various colored insoluble compounds or "lakes" with metallic oxides, the ones of chief importance being those of aluminum and tin (red), the iron (violet-black), and the lime (reddish-blue). The finest color obtained with alizarine, known as "Turkey red," is produced by mordanting the materials with acetate of alumina and treating them with a sulphonated castor oil, known as "Turkey red oil," before applying the alizarine.

By the reduction of alizarine with ammonia and zinc-dust is formed *desoxyalizarine*, $C_6H_4\langle\begin{matrix}C(OH)\\|\\CH\end{matrix}\rangle C_6H_2(OH)_2$, which, under the name of "anthrarobin," has been used in medicine

as a non-poisonous substitute for chrysarobin and chrysophanic acid.

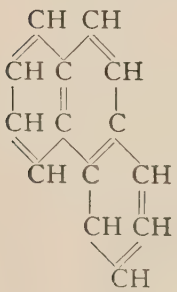
Purpurine (Trioxyanthraquinone), $C_{14}H_5(OH)_3O_2$.—This dye is found along with alizarine in madder-root, and is also prepared artificially.

A homologue of anthracene is also found in coal-tar,—viz., *Methyl-anthracene*, $C_{14}H_9(CH_3)$. It is capable of analogous reactions, yielding a quinone and hydroxyl derivatives of the same. The name of one of the latter is *Chrysophanic Acid* (Dioxy-methyl-anthraquinone), $C_{14}H_5(CH_3)(OH)_2O_2$. It is found in certain lichens, in yellow dock (*Rumex*), in senna, and in rhubarb. It crystallizes in golden-yellow prisms or needles, melting at 102°, and soluble in alcohol, ether, or benzene. Alkalies also dissolve it, forming dark-red solutions. When distilled over zinc-dust it yields methyl-anthracene.

Chrysarobin, U. S. P., which is found in Goa and araroba powder, has the formula $C_{20}H_{26}O_7$, and bears the same relation to chrysophanic acid that anthrarobin does to alizarine. It readily yields chrysophanic acid by its oxidation. It forms yellow scales or needles, melting at 170°–178°, is insoluble in water and ammonia, soluble in alkalies, with yellow color which gradually turns red, as on exposure to the air chrysophanic acid is formed. It is used like anthrarobin for external application in skin diseases.

Emodin (Trioxy-methyl-anthraquinone), $C_{15}H_{10}O_5$, occurs with chrysophanic acid in the bark of wild cherry and in rhubarb-root. When distilled with zinc-dust it also yields methyl-anthracene. It forms orange-red crystals, melting at 245°–250°.

2. **Phenanthrene**, $C_{14}H_{10}$, is an isomer of anthracene, and is also found in coal-tar. Its structural formula differs from that of anthracene, and is represented as $\begin{matrix} C_6H_4{-}CH \\ | \quad\quad \| \\ C_6H_4{-}CH \end{matrix}$, or more fully



, in which formula is shown the condensation

of three benzene nuclei, the middle one having two carbon atoms jointly with each of the side nuclei. It crystallizes in colorless, lustrous scales, melting at 99° and boiling at 340°. It may be separated from anthracene by fractional distillation, followed by repeated crystallization from alcohol, in which it is much more soluble than anthracene. It forms a crystalline compound with picric acid, crystallizing from benzene in yellow needles, melting at 145°, and soluble in hot alcohol without decomposition.

Phenanthrenquinone, $C_{14}H_8O_2$, is obtained by oxidizing phenanthrene by chromic acid mixture. It crystallizes in dark orange-yellow prisms, melting at 198°. When ignited with soda-lime it yields diphenyl, $(C_6H_5)_2$, in almost the theoretical proportions, whereas anthraquinone gives benzene when similarly treated.

The phenanthrene molecule is contained in the alkaloid morphine, as when this latter is distilled with zinc-dust phenanthrene is obtained.

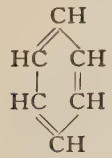
IV. Compounds containing Nitrogen in the Benzene Nucleus.

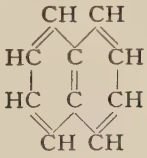
By the replacement of one triad group, CH, in the benzene molecule by the element nitrogen we obtain *Pyridine*, C_5H_5N.

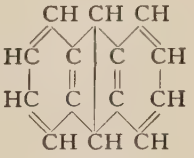
By the replacement of one triad group, CH, in the naphthalene molecule by the element nitrogen we obtain *Quinoline*, C_9H_7N.

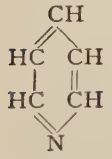
By the replacement of one triad group, CH, in the anthracene molecule by the element nitrogen we obtain *Acridine*, $C_{13}H_9N$.

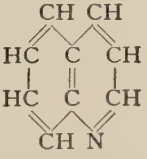
The relations of these nitrogenous bases to the parent hydrocarbons is shown clearly by a comparison of the graphic formulas:

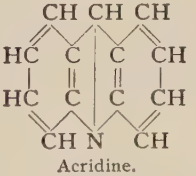

Benzene.


Naphthalene.


Anthracene.


Pyridine.


Quinoline.


Acridine.

1. **Pyridine Bases.**—Pyridine, C_5H_5N, and several of its

homologues are found in coal-tar and in the animal oils (Dippel's oil) obtained by the distillation of bones. They are also found in the products of the distillation of bituminous shales. Except that they are strong bases, they bear a great analogy to the aromatic hydrocarbons, and give rise to similar derivatives. Thus, they form acids, which when distilled with lime yield the pyridine again just as the aromatic acids yield benzene. This is seen in the comparison of reactions :

$$\underset{\text{Benzoic Acid.}}{C_6H_5.COOH} = \underset{\text{Benzene.}}{C_6H_6} + CO_2. \qquad \underset{\text{Pyridine Carboxylic Acid.}}{C_5H_4NCOOH} = \underset{\text{Pyridine.}}{C_5H_5N} + CO_2.$$

Hydrogen addition compounds form here just as in the case of benzene, and even more readily :

$$\underset{\text{Pyridine.}}{C_5H_5N} + H_6 = \underset{\text{Hexahydro-pyridine (or Piperidine).}}{C_5H_5N.H_6}.$$

Pyridine and its homologues may be built up synthetically by several reactions, among which the simplest is that whereby the aldehydes of the fatty series when treated with ammonia are made to yield these bases :

$$\underset{\text{Acetaldehyde.}}{4C_2H_4O} + NH_3 = \underset{\text{Collidine (Trimethyl-pyridine).}}{C_8H_{11}N} + 4H_2O.$$

More generally, however, they are obtained as decomposition products from more complex substances. Thus, both pyridine and quinoline bases are the products of the distillation of many alkaloids, such as quinine cinchonine, and strychnine, with potash, and the carboxylic acids of these bases from the oxidation of the same alkaloids. The relationship of the alkaloids to pyridine and quinoline will be referred to later under the individual alkaloids.

Because of the existence of the one nitrogen atom in the benzene nucleus we may have three isomeric mono-substitution derivatives, according to the position of the replacing group with reference to this nitrogen atom. Where the same replacing group enters twice in place of two hydrogen atoms of the nucleus we may have six isomeric derivatives.

Pyridine, C_5H_5N, may be obtained from coal-tar or in a pure state by distilling its carboxylic acid with lime. It is also present in commercial ammonia, and has been identified in tobacco-smoke. Colorless liquid, with penetrating, characteristic odor, boiling at 115°. Is readily miscible with water. By adding me-

tallic sodium to its hot alcoholic solution hydrogen is taken up and hexahydropyridine or piperidine is formed. On the other hand, heating to 300° with HI causes a reduction and decomposition whereby normal pentane is formed: $C_5H_5N + H_{10} = C_5H_{12} + NH_3$.

It is a strong base, throwing the hydrates of aluminum, chromium, and iron out of the solutions of the salts of these metals. It has been used in medicine as a remedy for asthma.

By the action of metallic sodium pyridine is polymerized, forming *dipyridine*, $C_{10}H_{10}N_2$, together with a compound analogous to diphenyl (see p. 782), known as *dipyridyl*, $C_{10}H_8N_2$.

Methyl-pyridines, $C_5H_4(CH_3)N$.—The three isomeric methyl-pyridines, known also as "picolines," are found in coal-tar. The β-compound may also be prepared from acroleïn-ammonia, or from strychnine, by distilling with lime. Liquids of unpleasant, penetrating odor.

Ethyl- and *Propyl-pyridines* are both known. The latter, we shall see, bears a close relation to the natural alkaloid conine. Thus, conyrine, $C_8H_{11}N$, which is obtained on heating conine with zinc-dust, and which yields conine again when treated with HI, is α-normal-propyl-pyridine.

Dimethyl-pyridines, $C_5H_3(CH_3)_2N$.—In bone-oil and tar-oil three isomeric compounds of this formula, known also as "lutidines," have been found.

Trimethyl-pyridines, $C_5H_2(CH_3)_3N$. — These compounds, known as "collidines," are found in bone-oil and obtained from cinchonine by heating with potash.

Pyridine-carboxylic Acids.—While pyridine itself is quite stable and resists the action of oxidizing agents, its homologues, like those of benzene, are very readily oxidized, yielding the corresponding carboxylic acids. Three mono-carboxylic acids, $C_5H_4N.COOH$, are known,—viz., α acid—*picolinic acid*, melting at 135°; β acid—*nicotinic acid*, melting at 231°; and γ acid—*iso-nicotinic acid*, melting at 309°. These acids may be obtained by the oxidation of the α-, β-, and γ-picolines respectively with potassium permanganate. The β acid is also obtained by the oxidation of the alkaloid nicotine by different oxidizing agents. On heating with lime the above acids yield pyridine, just as benzoic acid yields benzene under similar conditions.

Of the six possible di-carboxylic acids, $C_5H_3N.(COOH)_2$, all are known. The only ones requiring mention are *quinolinic acid*, obtained by the oxidation of quinoline and *cinchomeronic acid*,

the chief product of the oxidation of quinine by nitric acid, as well as from cinchonine along with other products. Of the pyridine-tricarboxylic acid, $C_5H_2N(COOH)_3$, two may also be mentioned: *hydroxycinchomeronic acid*, obtained from quinine, quinidine, and cinchonidine by boiling with an alkaline solution of potassium permanganate, and *berberonic acid*, obtained from berberine when oxidized by nitric acids.

Hydrogen-addition Products of Pyridine.—Just as benzene, C_6H_6, is capable of taking up six hydrogen atoms and yielding hexahydrobenzene, $C_6H_6.H_6$, so pyridine may take up six hydrogen atoms and yield hexahydropyridine or *piperidine*, $C_5H_5N.H_6$. This compound, in addition to being produced synthetically, as above mentioned, is obtained by the decomposition of the alkaloid piperin of pepper, which, under the influence of alcoholic potash, splits into piperidine and piperic acid. An important synthesis of piperidine is also that from pentamethylene-diamine, as shown:

$$\underset{\text{Pentamethylene-diamine}}{CH_2<\begin{matrix}CH_2—CH_2—NH_2\\CH_2—CH_2—NH_2\end{matrix}} = \underset{\text{Piperidine}}{CH_2<\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}>NH} + \underset{\text{Ammonia.}}{NH_3}.$$

Piperidine is a colorless liquid, boiling at 106°, easily soluble in water and alcohol, and of a peculiar peppery odor. It is a strong base, and forms crystallized salts.

Two of the natural alkaloids may be mentioned here, as they are hydrogen-addition derivatives of pyridine.

Conine, $C_8H_{17}N$, is *dextro-rotatory α-normal propyl-piperidine*, $C_5H_{10}N(C_3H_7)$. This is the poisonous principle of the hemlock (*Conium maculatum*), and is found chiefly in the seeds. Colorless liquid, of stupefying odor, boiling at 166°. Easily soluble in ether and alcohol, more difficultly in water. It has been made synthetically by Ladenburg from α-allyl-pyridine, which, reduced by sodium in alcoholic solution, yields an optically inactive, normal propyl-piperidine, and this by the crystallization of its tartrate is split into a dextro-rotatory variety (the true conine) and a lævo-rotatory variety. Hydrogen iodide reduces it at a high heat to normal octane, C_8H_{18}, while nitric acid oxidizes it to butyric acid.

Piperidine, as well as conine, can be methylated, and the products are known as methyl-piperidine and methyl-conine. The latter is also found in the hemlock with conine.

Nicotine, $C_{10}H_{14}N_2$, the alkaloid of tobacco, is *hexahydro-dipyridyl*, $C_{10}H_8(H_6)N_2$. It exists in the tobacco plant combined with malic and citric acids. Pure nicotine is a colorless, oily

liquid, turning brown in the air; soluble in water, alcohol, and ether, of stupefying odor, and boiling at 250° with decomposition. It is intensely poisonous. When oxidized yields nicotinic (β-pyridine-carboxylic) acid, and by loss of hydrogen dipyridyl, $(C_5H_4N)_2$.

Tropine, the decomposition product of the alkaloids Atropine and Hyoscyamine, is also a hydrogenated pyridine derivative.

Cocaine and *Ecgonine*, its decomposition product, are similarly derivatives of these hydrogenated pyridines.

2. Quinoline Bases.—By the dry distillation of organic substances, such as bituminous coal and bones, is produced a series of bases known by this name. The same bases are also obtained in the distillation of quinine and cinchonine with potash. A number of synthetic methods have also been found for their preparation, of which may be mentioned:

(*a*) By heating acroleïn-aniline quinoline is formed, just as the heating of acroleïn-ammonia yields pyridine.

(*b*) By the oxidation of allylaniline with heated oxide of lead:

$$C_6H_5.NH(C_3H_5) + O_2 = C_9H_7N + 2H_2O.$$

(*c*) By heating aniline with glycerin, concentrated sulphuric acid, and nitrobenzene. This method (discovered by Skraup) is that now employed for the manufacture of quinoline. 24 parts of nitrobenzene, 38 parts of aniline, 120 parts of glycerin, and 100 parts of concentrated sulphuric acid are taken and heated, at first carefully, and then for several hours with inverted condenser. The mixture is now diluted with water, and the nitrobenzene distilled off. Caustic soda is then added to strong alkaline reaction, and the quinoline distilled off in a current of steam. In this reaction the sulphuric acid first dehydrates the glycerin, producing acroleïn, which then unites with the aniline to form the quinoline molecule with the elimination of hydrogen. The nitrobenzene furnishes the oxygen to combine with this hydrogen, and is itself reduced to aniline. The reactions may be summarized thus:

$$2C_6H_5.NH_2 + C_6H_5.NO_2 + 3C_3H_8O_3 = 3C_9H_7N + 11H_2O.$$

By using the homologues of acroleïn in the first of these methods instead of acroleïn we obtain the homologues of quinoline, as methyl-quinoline (quinaldine), dimethyl-quinoline, etc.

The constitution of the quinoline molecule has already been referred to and illustrated. That it contains the benzene nucleus is shown by its syntheses from aniline and nitrobenzene; that it contains a pyridine nucleus joined with this is shown by the fact

that, when oxidized by potassium permanganate, quinoline yields pyridine-dicarboxylic (cinchomeronic) acid.

Quinoline, C_9H_7N, is a pale-yellowish liquid with considerable refractive power and a characteristic aromatic odor. It boils at 237°, and has a specific gravity of 1.084. Only slightly soluble in water, easily soluble in alcohol, ether, chloroform, and petroleum benzene. It is darkened in color on exposure to light. It is a base, and forms a series of crystallizable and deliquescent salts. Among these may be mentioned :

Quinoline Hydrochlorate, $C_9H_7N.HCl$, forms a colorless, deliquescent salt, easily soluble in water, with a biting and sharp taste.

Quinoline Tartrate, $3C_9H_7N.4(C_4H_6O_6)$. — This salt forms white, rhombic needles, which have a slight odor of bitter-almond oil, and taste sharp and peppermint-like. It is permanent in air, and fuses at 125°. It is moderately soluble in water, more difficultly soluble in alcohol, and almost insoluble in ether. It is extensively used in medicine as an antiseptic and antipyretic.

Quinoline Salicylate, $C_9H_7N.C_7H_6O_3$, forms a whitish, crystalline powder, not very soluble in water, easily soluble in alcohol, ether, benzene, vaseline, fats, and glycerin. It is used in medicine as the tartrate, and in similar amounts.

Homologues of Quinoline. — The methyl group may replace H in either the benzene nucleus or the pyridine nucleus of the quinoline molecule. The compounds so obtained are isomeric. Thus, the compound obtained by the replacement of a hydrogen atom of the pyridine nucleus by methyl is known as *quinaldine*, and is found in coal-tar. When oxidized by chromic acid it yields quinoline-carboxylic acid. On the other hand, the compound obtained by the replacement of a hydrogen atom of the benzene nucleus by methyl is known as *Toluquinoline*, and has only been obtained synthetically. When oxidized it yields pyridine-dicarboxylic acid. By heating quinaldine with phthalic anhydride and chloride of zinc is obtained a phthaleïn of the composition $C_6H_4\left\{\begin{matrix}CO\\CO\end{matrix}\right\}CH.C_9H_6N$. It is known as "quinoline yellow," and is insoluble in water, and difficultly soluble in alcohol. On sulphonation with fuming sulphuric acid is obtained a disulphonic acid, the sodium salt of which is known as "soluble quinoline yellow."

Oxy-quinolines.—Those derivatives which have the OH group replacing hydrogen of the benzene nucleus have a phenol-like

character, and unite with diazo salts to form azo dye-colors. On the other hand, those oxy-quinolines which contain the OH group in the pyridine nucleus are called *carbostyriles.*

Hydrogen Addition Compounds.—Nascent hydrogen from tin and hydrochloric acid produces *dihydro-quinoline*, C_9H_9N, melting at 161°, and a liquid *tetrahydro-quinoline*, $C_9H_{11}N$, boiling at 245°. By the action of methyl iodide upon this latter is obtained *methyl-tetrahydro-quinoline*, the acid sulphate of which was introduced into medicine as an artificial febrifuge under the name of "kairoline."

Similarly, the oxy-quinoline before mentioned is converted by the action of tin and hydrochloric acid into *oxy-tetrahydro-quinoline*, and by the action of either methyl or ethyl iodide upon this were obtained bases of febrifuge power. The hydrochlorate of ethyl-oxytetrahydro-quinoline was known as "kairine A," and that of methyl-oxytetrahydro-quinoline as "kairine M." They were, perhaps, the first of the artificial febrifuges, but are no longer in use, being accompanied by injurious after-effects.

Isomeric with the methyl-oxytetrahydro-quinoline, $C_9H_9(OH)$-$N.CH_3$, is the base *tetrahydro-paraquinanisol*, $C_9H_{10}(OCH_3)N$, the sulphate and tartrate of which have been introduced into medicine under the name of "thalline," because of the emerald-green color produced in its solution by ferric chloride. It is used as an antipyretic, antiseptic, and antifermentative.

Other quinoline derivatives that have been proposed for use in medicine are "diaphtherine," a compound of one molecule of orthophenol-sulphonic acid (aseptol) with two molecules of ortho-oxy-quinoline; "analgene," *ethyoxy-ana-monobenzoyl-amido-quinoline*, $C_9H_5(OC_2H_5).NH.COC_6H_5.N$, recommended as a febrifuge and antineuralgic; and "orexine," the chlorhydrate of phenyldihydro-quinazoline, $C_{14}H_{12}N_2.HCl + 2H_2O$, which has been recommended as a stomachic and stimulant to digestion.

Quinoline-carboxylic Acids.—Among the mono-carboxylic acids of the formula $C_9H_6N.COOH$ may be mentioned *quinaldinic acid*, obtained by oxidizing quinaldine and *cinchoninic acid*, obtained by oxidizing cinchonine with potassium permanganate or nitric acid. When distilled with lime it yields quinoline.

Kynurenic Acid is an oxy-quinoline-carboxylic acid. It occurs in the urine of dogs. *Quininic Acid*, $C_9H_5(OCH_3)N.COOH$, is the methyl-phenol ether of another oxy-quinoline-carboxylic acid. It is obtained by oxidizing quinine and quinidine with chromic

acid in sulphuric acid solution. Quinoline-dicarboxylic acids, $C_9H_5N(COOH)_2$, are also known.

3. **Acridine and its Derivatives.**—Acridine, $C_{13}H_9N$, has already been explained and its relationship to anthracene stated (see p. 795). It is found in coal-tar and in the crude anthracene extracted therefrom. It has been made synthetically from diphenylamine, formic acid, and zinc chloride:

$$C_6H_5{-}NH{-}C_6H_5 + HCOOH = C_6H_5{-}\underset{\displaystyle N}{\overset{\displaystyle CHO}{|}}{-}C_6H_5 + H_2O.$$

Diphenylamine + Formic Acid = Formyl-diphenylamine.

This compound then breaks up into acridine and water:

$$C_6H_5{-}\underset{\displaystyle N}{\overset{\displaystyle CHO}{|}}{-}C_6H_5 = C_6H_4\underset{\displaystyle N}{\overset{\displaystyle CH}{|}}C_6H_4 + H_2O.$$

Acridine.

It forms colorless needles or scales, fusing at 107°–111°. Scarcely soluble in water, easily soluble in ether, alcohol, benzene, carbon disulphide, etc. It is a base, and dissolves in dilute acid with a beautiful green fluorescence. Acridine irritates the skin and mucous membranes, whence the name. Among its derivatives are several important dye-colors, such as *chrysaniline*, which is the nitrate of diamido-phenylacridine, and *benzoflavine*, which is an isomer of the other.

CHAPTER VIII.

THE ALKALOIDS AND PTOMAINES.

The term alkaloid has been applied to a number of physiologically active principles occurring in the vegetable kingdom, and this common occurrence was emphasized more than any general chemical character. It is true it was recognized that they were nitrogenous, and that they acted as derived ammonias in their method of forming salts, but for a long time nothing more definite could be said with regard to their chemical nature. It is now recognized that, while the great majority of these are derivatives of the basic compounds pyridine and quinoline, just noticed in the preceding pages, there are also methane derivatives among them, as caffeine and theobromine, which are related to uric acid, and that, besides the occurrence of these important bases in the plant kingdom, substances answering to many of the alkaloid tests are produced in the decay of animal tissue, giving rise to the so-called "cadaveric alkaloids," or ptomaïnes. It remains true of all these classes, however, that we have to do with derived ammonias, either amines or amides, and this feature, together with their physiological activity, must be taken to constitute the basis of their claim to the name alkaloid, whether synthetically formed, as conine now can be, or found in the vegetable or animal kingdom only. The termination *ine* has been made uniform for them as expressing their basic character and their derivation from ammonia.

Classification of the Alkaloids.—Leaving the animal alkaloids for subsequent consideration, we find that the vegetable alkaloids may be divided into two classes : those which are liquid and volatile, and those which are solid and non-volatile. At the same time we find that with this physical distinction corresponds a difference in chemical composition,—viz., the liquid alkaloids do not contain oxygen, while the solid alkaloids are oxygenated bases. As the liquid alkaloids are very limited in number, no further grouping is necessary for them. For the solid alkaloids it will be found convenient to group them in addition according to the order or family of plants in which related alkaloids are found.

Extraction of Alkaloids from the Plants.—The vegetable alkaloid does not ordinarily exist in the plant in a free state. It is most generally present as a salt, often an acid salt of some organic acid, such as malic or tannic acid. We have also some as salts of organic acids peculiar to the particular plant, such as meconic acid in opium, quinic acid in cinchona bark, and igasuric acid in *nux vomica*. Inorganic acids are also occasionally found in combination with the alkaloids, as in opium, where the morphine is combined as sulphate. While most of these naturally occurring alkaloidal salts are soluble in water, others, such as the tannates, are not, so that for their extraction from the plants dilute acids are generally used. At times, though, the alkaloid is liberated from its combination in aqueous infusion by the aid of lime or magnesia, and then extracted by ether, chloroform, or alcohol. The extraction is also accomplished at times by alcohol used directly upon the finely powdered or comminuted plant, as most of the alkaloidal salts are easily soluble in it. In this case the solvent is removed by gentle evaporation or distillation before proceeding to further purification of the alkaloid.

Alkaloidal Reagents.—Under this head we may consider the two classes,—those which act as *precipitants*, and those which give distinctive *color-tests*. Among the precipitants we note, first, *tannic acid*. The tannates of the alkaloids are mostly difficultly soluble in cold water, so that the addition of tannic acid precipitates them from aqueous solution of either free alkaloid or its salt even quite dilute; the precipitates are soluble in excess of the tannic acid, and in other acids and alcohol; often, indeed, in hot water. Second, the haloid salts of mercury and some other metals tend to form difficultly soluble precipitates with the alkaloids. Thus, *corrosive sublimate* alone, or *potassium iodohydrargyrate* (Mayer's reagent), together with the corresponding double salts, *potassium cadmium iodide* (Marmé's reagent) and *potassium bismuth iodide* (Dragendorff's reagent), all have the power of precipitating in greater or less degree the alkaloid in the form of a double salt. Indeed, *iodized iodide of potassium* (Bouchardat's or Wagner's reagent) will produce insoluble precipitates with the great majority of alkaloids. Third, *picric acid* (Hager's reagent) precipitates a number of the alkaloids, such as the cinchona bases, from solution of the salts or the free bases. Fourth, *phosphomolybdic acid* (Sonnenschein's reagent) and *phosphotungstic acid* (Scheibler's reagent) are available as precipitants for the great majority of alkaloids. Fifth, neutral

potassium chromate, as well as the *bichromate*, precipitates from the concentrated aqueous solutions of their salts most of the alkaloids in the form of difficultly soluble chromates. From dilute solutions, however, the neutral chromate precipitates often the free alkaloid. Sixth, both *gold chloride* and *platinic chloride* form well-crystallized double salts with many of the alkaloids, which serve for their separation and purification.

The color-tests with alkaloids are at times very strong, but are not sufficiently distinctive or exclusive in character to be depended upon for decisive determination of the alkaloids. They are easily interfered with in most cases by the presence of a third substance, and can only be of value when compared with the same test applied to a sample of the same alkaloid of known purity. These color-reactions are thus classified by A. H. Allen:* (1) Those produced by dehydrating agents, such as strong sulphuric acid, phosphoric oxide, and zinc chloride; (2) those given by oxidizing agents not of themselves yielding colors, such as nitric acid, chlorine, bromine, and bleaching powder; or sulphuric acid and oxidizing agents, such as potassium chlorate, perchlorate, and permanganate; (3) those given by oxidizing agents which themselves yield a colored product by reduction, such as iodic acid and reagents containing chromic, molybdic, tungstic, and vanadic acids; (4) and colorations produced by certain special reagents, such as ferric chloride, hydrochloric acid, sulphuric acid and sugar, etc.

The most important and characteristic of these color-tests will be given later under the heads of the individual alkaloids.

Detection and Extraction of the Alkaloids from Mixtures.

1. Method of Stas and Otto.—The first general process for the extraction of the alkaloids from various complicated mixtures in which they may occur was that of Stas as modified by Otto in 1856. The material supposed to contain the alkaloids is extracted by alcohol with the addition of tartaric acid, and the residue obtained by the careful evaporation of this liquor is shaken with ether. In this extract may be colchicine. The portion insoluble in ether is now made alkaline and again shaken with ether. In this second ether extract may be found conine, nicotine, strychnine, quinine, atropine, etc. The alkaline solution containing

* Com. Org. Anal., vol. iii., Part ii., p. 44.

soda is then treated with ammonium chloride, and shaken with amyl alcohol in order to extract morphine. The solution containing ammonium chloride is evaporated and extracted with strong alcohol, which may yield solanine, berberine, etc. This method of Stas and Otto was next modified by Rodgers and Girdwood, who employed chloroform instead of ether, and by Uslar and Erdmann, who recommended the use of amyl alcohol.

2. **Method of Dragendorff.**—This method is the most comprehensive one as yet proposed, and is in most general use. It is given in outline: The material to be investigated is extracted with dilute sulphuric acid. The extract which contains the alkaloids as sulphate is evaporated and precipitated with alcohol. It is then filtered and the alcoholic filtrate evaporated. The acid solution is then extracted in succession with petroleum ether, benzene, and chloroform. The portion undissolved is made alkaline with ammonia and then extracted in succession with petroleum ether, benzene, chloroform, and amyl alcohol. Seven extractions are thus made, which may be tabulated as follows:

I. Extractions from acid solutions:
   (*a*) With petroleum ether: piperine, and, in addition, carbolic, salicylic, and picric acids.
   (*b*) With benzene: cantharidin and digitalin, berberine and colchicine.
   (*c*) With chloroform: narcotine, picrotoxin, and digitaleïn.

II. Extractions from alkaline solutions:
   (*a*) With petroleum ether: nicotine, conine, quinine, and some strychnine.
   (*b*) With benzene: quinine, atropine, cocaïne, strychnine, brucine, veratrine, and thebaïne.
   (*c*) With chloroform: a little morphine, papaverine.
   (*d*) With amyl alcohol: morphine, solanine, narceïne.

3. **Sonnenschein's Method.**—In this method the material is acidified with dilute hydrochloric acid, and then phosphomolybdic acid is added, which precipitates all the alkaloids. The precipitate is warmed with baryta water, when the volatile alkaloids may be distilled off. The solution, after filtering off the barium precipitates, is freed from barium by addition of carbon dioxide, and the aqueous solution is then investigated by the methods of either Stas-Otto or Dragendorff. The objection to this method is that the treatment with barium hydrate may cause decomposition in some of the active principles present.

4. **Method of Brieger.**—This is chiefly for the separation of the ptomaïnes if present in a suspected mixture. The solution is treated with hydrochloric acid to convert the bases into chlorides, and then, after a preliminary clarifying of the solution, if necessary, with lead acetate, the ptomaïnes are precipitated with mercuric chloride solution. Most of these bases are thus thrown out (tetanine is an exception), and, after suspending the mixture in water and freeing it from mercury by hydrogen sulphide, the ptomaïnes are obtained in the form of double salts with gold and platinic chlorides, and tested by experiments upon animals.

The special description of the more important alkaloids can now be taken up on the basis of the simple classification before made.

Volatile Alkaloids.

As the simplest of the naturally occurring alkaloids may be mentioned *methylamine* and *trimethylamine*, both of which are found at times in the vegetable kingdom, as well as in the products of decomposition of animal tissues. They have already been noted and their varied occurrence detailed (see p. 682).

Piperidine, $C_5H_5N.H_6$, has been found naturally occurring in pepper as a decomposition-product of piperine. It has already been described under the name of hexahydropyridine (see p. 798).

Conine, $C_8H_{17}N$ (or $C_5H_{10}(C_3H_7)N$).—This has also been referred to as α-normal-propyl-piperidine, or rather the dextrorotatory variety of the same, having been made synthetically by Ladenburg.

Conine is the poisonous alkaloid of the hemlock (*Conium maculatum*), and is an oily liquid of a peculiar repulsive odor. It is colorless when freshly prepared, but becomes yellow and ultimately resinoid on keeping. It is soluble in about 90 parts of water, and is readily dissolved by alcohol, acetone, amylic alcohol, ether, chloroform, petroleum ether, and benzene. It is a strong base and neutralizes acids perfectly. By the treatment of conine with chromic-acid mixture, normal butyric acid is produced. The reaction may be employed as a test for conine, as butyric acid is readily recognized by its odor.

Associated with conine in the conium are the following less important bases: *Conhydrine*, $C_8H_{17}NO$; *pseudo-conhydrine*, isomeric with the former; *methylconine*, $C_9H_{19}N$, and *ethylpiperidine*, $C_7H_{15}N$.

Conine is an extremely powerful paralytic poison, which acts on the motor nerves; one drop is a distinctly poisonous dose, while ten drops may be fatal.

Nicotine, $C_{10}H_{14}N_2$.—This alkaloid has been referred to and stated to be hexa-hydro-dipyridyl. It is the poisonous principle of tobacco, in which it exists combined with malic and citric acids in amounts ranging from about 1 per cent. to 7 per cent. of the dry leaf. The nicotine is a colorless, oily liquid of sp. gr. 1.011 at 15°, which on prolonged exposure to air becomes yellow and ultimately resinous. It has a strong and unpleasant odor, recalling that of tobacco, a sharp, caustic taste, and is intensely poisonous. It is soluble in water and alcohol, but is extracted from its aqueous, alkaline solutions by agitation with ether, chloroform, benzene, amyl alcohol, or petroleum naphtha. Nicotine is precipitated by Mayer's reagent from very dilute solutions. On adding mercuric chloride to a solution of nicotine, a white, crystalline precipitate is produced, soluble in dilute hydrochloric or acetic acid. This is the most characteristic reaction of nicotine. From conine, nicotine is distinguished by its odor, by being heavier instead of lighter than water, and by its reactions with mercuric chloride, platinic chloride (yellowish, crystalline precipitate), and picric acid (yellow, amorphous precipitate turning crystalline). The poisonous effects of tobacco when taken into the stomach, it is agreed, are entirely due to the nicotine. When tobacco is smoked, the greater part of the nicotine is converted into pyridine and other decomposition-products; some, however, escapes decomposition, as Melsens has proved the presence of unchanged nicotine in tobacco smoke in a proportion equal to about one-seventh of that present in the original tobacco. Vohl and Eulenberg have concluded from their experiments that the intense action of tobacco smoke on the nervous system is not due to nicotine at all, but to the presence of the bases of the pyridine series.

Piturine, $C_{12}H_{16}N_2$.—The volatile alkaloid of pituri (the dried leaves of *Duboisia Hopwoodii*, a shrub growing in Australia) was regarded by Petit as identical with nicotine, but its individual character was established by Liversidge. In chemical characters and physiological effects it bears a close resemblance to nicotine, but can be distinguished by gently warming it with hydrochloric acid. Nicotine so heated turns violet, while piturine does not change at all.

Lobeline is the active principle of *Lobelia inflata*, or Indian tobacco. Paschkis and Smita obtained the alkaloid as a viscous oil with an odor at once resembling honey and tobacco.

Sparteine, $C_{15}H_{26}N_2$, is obtained from the coarsely-powdered leaves and branches of broom (*Spartium scoparium*). It is a colorless, oily liquid, boiling at 287°. It has a somewhat pungent, pyridine-like odor, a very bitter taste, and on exposure to air turns brown and thick. It is soluble in alcohol, ether, and chloroform, but insoluble in petroleum ether. When oxidized with potassium permanganate it yields a volatile acid, together with a non-volatile, pyridine-carboxylic acid, which distilled with lime yields pyridine.

Spigeline is the active principle of *Spigelia Marylandica*, or "pink-root." It was obtained as a volatile alkaloid on distilling the root with milk of lime.

Non-Volatile Alkaloids.

1. The Belladonna Alkaloid Group.—A series of natural alkaloids exist in the plants of the family *Solanaceæ*, and have been named atropine and belladonine, from the *Atropa belladonna*, hyoscyamine and hyoscine, from *Hyoscyamus niger*. The supposed daturine, from *Datura stramonium*, and duboisine, from *Duboisia myoporoïdes*, have been shown to be identical with atropine and hyoscyamine respectively. All of these bases are distinguished by a remarkable power of dilating the pupil, and hence are often termed the "mydriatic alkaloids." The three bases, atropine, hyoscyamine, and hyoscine, are, moreover, all isomeric, and hyoscyamine, it is found, is converted into atropine by prolonged heating above its fusing point or by the action of alkalies.

Atropine (Daturine), $C_{17}H_{23}NO_3$, **Atropina**, U. S. P., belongs to the class of tropeïnes, or compounds of the base *tropine*, $C_8H_{15}NO$. When the natural alkaloid is heated with hydrochloric acid or baryta water, it is decomposed (saponified) according to the reaction :

$$\underset{\text{Atropine.}}{C_{17}H_{23}NO_3} + H_2O = \underset{\text{Tropine.}}{C_8H_{15}NO} + \underset{\text{Tropic Acid.}}{C_9H_{10}O_3}.$$

The preferable method of effecting the saponification of these alkaloids is to heat the alkaloid with saturated baryta water to 60° or 80° for a few hours. When the hydrolysis is effected by an acid, especially concentrated hydrochloric acid, the tropic acid loses the elements of water, and atropic acid, $C_9H_8O_2$, results. On the other hand, the tropic acid and tropine resulting from the hydrolysis of either atropine or hyoscyamine, when heated together at 100° with dilute hydrochloric acid, regenerate atropine.

Pure atropine forms white, acicular crystals, without odor, having a bitter, acrid taste, and gradually becoming yellowish on

exposure to the air. It melts when pure at 115°, but the commercial article melts at 108°. It is difficultly soluble in cold water, easily soluble in alcohol, ether, and chloroform. It is optically inactive, although a dextro-rotatory and a lævo-rotatory variety can be obtained synthetically. It is a powerful poison, producing delirium and convulsions.

Of its salts the sulphate is the most important (**Atropinæ Sulphas,** U. S. P.), but the borate and valerate are also used in ophthalmic surgery.

Hyoscyamine (Duboisine), $C_{17}H_{23}NO_3$, occurs with atropine in *Atropa belladonna*, and with hyoscine in the several species of *Hyoscyamus*. It is isomeric with atropine, and is readily converted into it. Ladenburg holds that the inactive atropine stands to the active hyoscyamine in the same relation as racemic acid stands to lævo-tartaric acid. It forms slender, colorless needles, melting at 108.5°. It shows an optical rotation of —29°. When decomposed by baryta water it yields the same products as atropine.

Of its salts the hydrobromate (**Hyoscyaminæ Hydrobromas,** U. S. P.) and sulphate (**Hyoscyaminæ Sulphas,** U. S. P.) are official.

Hyoscine, $C_{17}H_{23}NO_3$, is an amorphous base occurring with hyoscyamine in henbane. When saponified it yields tropic acid and pseudatropine, a base isomeric with tropine, but melting at 106° instead of 61°–62°. It is more rapid and powerful in its mydriatic effects than either atropine or hyoscyamine. Of its salts one only is official (**Hyoscinæ Hydrobromas,** U. S. P.).

Belladonine, $C_{17}H_{21}NO_2$ (according to Ladenburg, $C_{17}H_{23}NO_4$), and *Atropamine*, its isomer, are considered as anhydro-bases, and occur naturally with the other bases.

Artificial Tropeïnes.—When tropine, $C_8H_{15}NO$, is treated with certain acid chlorides, like benzoyl chloride, or evaporated to dryness with the acids referred to, together with dilute hydrochloric acid, we have formed esters of the base tropine with the several acid radicals. Thus, we have formed *benzoyl-tropeïne*, *salicyl-tropeïne*, and, with mandelic acid (see p. 778), *homatropine*, $C_{16}H_{21}NO_3$. The last-mentioned artificial alkaloid has the formula of a lower homologue of atropine, and has the same mydriatic action, which, however, is shorter in its duration. The homatropine crystallizes from absolute ether in prisms, which melt at 98°, and are very deliquescent. Its hydrobromate is official as **Homatropinæ Hydrobromas,** U. S. P.

2. The Cinchona Alkaloids.—The barks of the *Cinchona Calisaya*, *Cinchona officinalis*, and of hybrids of these, are, according to the U. S. Pharmacopœia, the sources of quinine and its associated alkaloids, containing not less than 5 per cent. of total alkaloids, of which 2.5 per cent. is quinine. The maximum percentage of quinine seems to have been reached in the *Cinchona Ledgeriana*, grown in Java in 1876, which yielded 13.25 per cent. of quinine. These barks contain some 32 natural alkaloids, and in the processes of extraction and purification some 8 additional bases are formed by alteration of the naturally occurring ones.

The list of naturally occurring cinchona alkaloids, as given by **A. H. Allen**, on the authority of **Paul and Cownley**, is as follows:

I. *Cinchonine class:*
- Paricine, $C_{16}H_{18}N_2O$.
- Cinchotine, $C_{19}H_{24}N_2O$.
- Cinchonamine, "
- Hydrocinchonine, "
- Hydrocinchonidine, "
- Cinchonine, $C_{19}H_{22}N_2O$.
- Cinchonidine, "
- Homocinchonidine, "
- Cinchonicine, "
- Paytine, $C_{21}H_{24}N_2O$.
- Paytamine, "

II. *Quinamine class:*
- Quinamine, $C_{19}H_{24}N_2O_2$.
- Conquinamine, "
- Javanine, ——.
- Cupreine, $C_{19}H_{22}N_2O_2$.

III. *Quinine class:*
- Hydroquinine, $C_{20}H_{26}N_2O_2$.
- Hydroquinidine, "
- Quinine, $C_{20}H_{24}N_2O_2$.
- Quinidine, "
- Quinicine, "

IV. *Cusconine class:*
- Chairamine, $C_{22}H_{26}N_2O_4$.
- Conchairamine, "
- Chairamidine, "
- Conchairamidine, "
- Concusconine, "
- Aricine, $C_{23}H_{28}N_2O_4$.
- Cusconine, $C_{23}H_{26}N_2O_4$.
- Cusconidine, "
- Cuscamine, ——.
- Cuscamidine, ——.

V. *Anhydro-bases:*
- Dicinchonicine, $C_{38}H_{44}N_4O_2$.
- Diquinicine, $C_{40}H_{46}N_4O_3$.

Of all this list, however, four stand out as more important, and all four are represented among official compounds. These four are *quinine* and *quinidine*, which are isomers with the formula $C_{20}H_{24}N_2O_2$, and *cinchonine* and *cinchonidine*, isomers with the formula $C_{19}H_{22}N_2O$.

In the free state these alkaloids are colorless or slightly yellowish solids, fusible but not volatile without decomposition. They are generally but slightly soluble in water, but more readily soluble in alcohol, and generally quite soluble in ether and chloroform. When soluble in these last two liquids, they may be

removed from their ammoniacal solutions by agitation with ether or chloroform, but these solvents will not remove them from an aqueous solution acidified with sulphuric or hydrochloric acid. The anhydrous sulphates of several of the cinchona alkaloids, however, are soluble in chloroform, and still more readily in a mixture of chloroform and absolute alcohol. Solutions of some of the cinchona alkaloids in excess of dilute sulphuric acid exhibit a strong blue fluorescence which is visible even in very dilute liquids. This fluorescence is destroyed by adding an excess of chloride of sodium or other haloid salt.

The solutions of the cinchona alkaloids all show optical activity, quinine and cinchonidine being lævo-rotatory and cinchonine and quinidine being dextro-rotatory.

The sulphates of several of the cinchona bases possess the property of combining with iodine, forming "iodosulphates." Some of these, as herapathite (quinine iodosulphate), have the power of polarizing light like tourmaline (see p. 105).

Certain of the cinchona bases give a deep-green coloration when their solutions are treated with chlorine or bromine water and ammonia is subsequently added, a reaction known as the "thalleioquin test."

Quinine, $C_{20}H_{24}N_2O_2$ (**Quinina, U. S. P.**), is the most important of these bases, and apparently possesses the most powerfully febrifuge properties. The free base may be obtained either anhydrous, as a white, flaky, amorphous powder, melting at 173°, and readily becoming resinous, or as a crystalline powder containing 3 molecules of water of crystallization. It then melts at 57° and loses its water gradually, the last disappearing at 125°. It is odorless and has an intensely bitter taste. It is very sparingly soluble in water, readily soluble in alcohol and anhydrous ether, in chloroform, benzene, petroleum naphtha, and carbon disulphide, the anhydrous base being in all cases more readily soluble than the hydrate. The reactions for quinine which are most distinctive are: First, the strong blue fluorescence which its solutions in dilute sulphuric acid exhibit; even the salts with haloid acids show this when an excess of dilute sulphuric acid is added. Quinidine will also show this fluorescence, but neither cinchonine and its isomers nor cupreine show it. Second, a solution of quinine, as nearly neutral as possible, is treated with either chlorine or bromine, and then with excess of ammonia, when a green substance called "thalleioquin" is produced. In concentrated solutions a precipitate is formed, and in dilute ones

a deep-green coloration only. The thalleioquin reaction is also given by quinidine and cupreine, but not by cinchonine and its isomers. It is prevented by morphine. Third, on adding tincture of iodine to a solution of acid sulphate of quinine in dilute alcohol, a compound is produced known as *Herapathite*, of the composition $4C_{20}H_{24}N_2O_2,3H_2SO_4,2HI,I_4 + 3H_2O$. This body, called also "iodo-sulphate of quinine," is the type of a series of similar compounds formed by the action of iodine on the sulphates of the cinchona bases. It is only slightly soluble in water or dilute alcohol, but is soluble in boiling alcohol of 92 per cent., and is deposited on cooling in tabular crystals which are dichroic, and, as before stated, when in thin sections have the power of polarizing light. Herapathite is reconverted into quinine sulphate by treatment with sulphurous acid, thiosulphates, hydrogen sulphide, and other reducing agents. As the iodosulphate of quinine is much less soluble than the corresponding compounds of the other cinchona bases,* it has been proposed by de Vrij as a basis for the determination of quinine.

While the complete synthesis of quinine has not as yet been effected, it has been made from the accompanying alkaloid cupreine of the *Cinchona cuprea*. When cupreine in methyl alcohol solution is treated with metallic sodium and methyl chloride in a sealed tube under pressure, the following reaction takes place:

$$\underset{\text{Cupreine-sodium.}}{C_{19}H_{23}N_2O.ONa} + CH_3Cl = NaCl + \underset{\text{Quinine.}}{C_{19}H_{21}N_2O.OCH_3}.$$

Two basic substances isomeric with quinine have also been made synthetically: one, discovered by C. A. Kohn, was prepared by acting on hydroxy-hydroquinoline with ethylene dibromide, and has the formula $C_9H_{10}(OH)N.C_2H_4.NC_9H_{10}(OH)$; the other was prepared by Wallach and Otto by the action of β-naphthylamine on pinol nitrosochloride, according to the reaction:

$$C_{10}H_7NH_2 + C_{10}H_{16}O.NOCl = HCl + C_{20}H_{24}N_2O_2.$$

The salts of quinine that are official at present are the sulphate, the bisulphate, the hydrobromate, the hydrochlorate, and the valerianate. With reference to the first named two it is necessary to note that the cinchona bases form two classes of sulphates, — viz., neutral sulphates, with the general formula

* The solubilities of the iodosulphates of the principal cinchona alkaloids in acidulated alcohol at 15° are as follows: Quinine herapathite, 1 in 255 parts; cinchonidine herapathite, 1 in 92 parts; quinidine herapathite, 1 in 61 parts; cinchonine, 1 in 42 parts.

$R_2H_2SO_4$, and acid or bisulphates, with the formula RH_2SO_4. The former of these have a neutral reaction to litmus and methyl-orange, and are in general sparingly soluble in water, while the second class are generally readily soluble.

Quinine Sulphate, $(C_{20}H_{24}N_2O_2)_2H_2SO_4.7H_2O$ (**Quininæ Sulphas**, U.S.P.).—This, the staple salt of quinine, is generally made on a large scale direct from the cinchona barks. For its preparation the following process, differing but slightly from that given in the U. S. Pharmacopœia of 1870, may be used.

Because of the fact that the naturally occurring salts of the alkaloid, the quinate and quino-tannate, are only moderately soluble, the powdered bark is repeatedly extracted with cold water acidified with dilute sulphuric acid. The several extraction-liquors are then united, supersaturated with milk of lime, and the precipitate, consisting of the cinchona bases, the calcium salts of sulphuric, quino-tannic, quinic, and quinovic acids and other substances, is washed, pressed, and slowly but completely dried. This dry precipitate is then repeatedly boiled with strong alcohol, and the clear extraction-liquid allowed to cool to separate a portion of the difficultly soluble cinchonine. The liquid separated from these crystals is then exactly neutralized with sulphuric acid and the alcohol distilled off. On cooling, there separates out the greater part of the quinine sulphate, which is difficultly soluble in water and dilute alcohol, while the more soluble sulphates of cinchonine, cinchonidine, quinidine, quinamine, etc., with a small quantity of quinine sulphate, remain in the mother liquor. To further purify the separated quinine sulphate, after pressing, it is dissolved in boiling water, decolorized with a little bone-black, and the solution allowed to stand again to crystallize. This operation may be repeated, if necessary. The quinine sulphate remaining in the mother liquor may be recovered by evaporating the solution to dryness, decomposing the sulphate with sodium carbonate, washing the free base which separates, dissolving it in the amount of dilute sulphuric acid needed for exact neutralization, and crystallizing it out.

Instead of using ethyl alcohol for the extraction, kerosene oil has been used in England, and amyl alcohol (fusel oil) quite extensively in this country.

The official sulphate forms loose, white, needle-like crystals of a somewhat silky lustre, which, however, is easily impaired by its tendency to lose water of crystallization and effloresce superficially. It is odorless, but of a persistent, very bitter taste.

Quinine Acid Sulphate, $C_{20}H_{24}N_2O_2,H_2SO_4.7H_2O$ (**Quininæ Bisulphas**, U. S. P.), is readily formed by dissolving quinine sulphate in the calculated amount of dilute sulphuric acid. It forms colorless, transparent, rhombic crystals of a bitter taste. It is soluble in 10 parts of water, forming a solution which fluoresces strongly blue and shows acid reaction. It loses its water of crys-

tallization at 100° C., and at 135° it melts and is converted into the isomeric quinicine bisulphate, which in dilute sulphuric acid solution has a yellow color but no blue fluorescence.

Quinine Hydrobromate, $C_{20}H_{24}N_2O_2,HBr.H_2O$ (**Quininæ Hydrobromas**, U. S. P.), forms light, white, silky needles, odorless, but with a very bitter taste. It is soluble in 54 parts of water at 15°. The salt is neutral or faintly alkaline. The aqueous solution when acidulated with sulphuric acid shows a fine blue fluorescence.

Quinine Hydrochlorate, $C_{20}H_{24}N_2O_2,HCl.2H_2O$ (**Quininæ Hydrochloras**, U. S. P.), forms white, silky, asbestos-like crystals which become anhydrous at 120°. It is soluble in 34 parts of water at 15° and in 3 parts of alcohol. The dilute, aqueous solution shows some little fluorescence, which becomes stronger on adding dilute sulphuric acid.

Quinine Valerianate, $C_{20}H_{24}N_2O_2,C_5H_{10}O_2.H_2O$ (**Quininæ Valerianas**, U. S. P.), forms colorless, triclinic plates, having a pearly lustre and a faint odor of valeric acid. It is not deliquescent. It is soluble in 100 parts of water at 15° and in 5 parts of alcohol.

Ferri et Quininæ Citras, U. S. P., and **Ferri et Quininæ Citras Solubilis**, U. S. P., are official scale preparations.

Quinidine (Conquinine), $C_{20}H_{24}N_2O_2$, is an isomer of quinine, and occurs frequently in cinchona barks. It is present to a considerable extent in commercial "quinoidine" (chinoidine). The free base crystallizes from alcohol in large, monoclinic, efflorescing needles, containing 2½ molecules of water. It gives the thalleioquin reaction like quinine and shows a blue fluorescence in dilute sulphuric-acid solution, but is dextro-rotatory and is sparingly soluble in ether, two points of difference.

Quinidine Sulphate $(C_{20}H_{24}N_2O_2)_2H_2SO_4.2H_2O$ (**Quinidinæ Sulphas**, U. S. P.), crystallizes in white, silky needles or prisms, which require 100 parts of water or 8 parts of alcohol for solution. This salt differs from the sulphates of the other cinchona alkaloids in requiring a temperature of 120° to render it anhydrous, and in readily taking up the water again in moist air.

Cinchonine, $C_{19}H_{22}N_2O$ (**Cinchonina**, U. S. P.).—This base is invariably present in cinchona barks. When the bases are crystallized from alcohol, the cinchonine, being the least soluble, deposits first. It crystallizes in anhydrous, shining prisms or needles, which melt at 165°. It is almost insoluble in cold water, requiring 3760 parts at 15° and 3500 parts at a boiling tempera-

ture, and is difficultly soluble in alcohol and ether, the best solvent being amyl alcohol or a mixture of amyl alcohol and chloroform. It does not give the thalleioquin reaction, its dilute sulphuric acid solutions do not fluoresce blue, and it is dextrorotatory, which characters, together with its difficult solubility in ether, distinguish it from quinine. When heated to a high temperature with an alkali, cinchonine yields quinoline, C_9H_7N, together with other products.

Cinchonine Sulphate $(C_{19}H_{22}N_2O)_2H_2SO_4.2H_2O$ (**Cinchoninæ Sulphas,** U. S. P.), forms short, hard, and shining, monoclinic prisms. Soluble in 54 parts of water at 15°, with a weak, alkaline reaction. Loses its water of crystallization at 100°, and melts with partial decomposition at 240°.

Cinchonidine, $C_{19}H_{22}N_2O$, is contained in several species of cinchona, but is especially characteristic of the red bark of *C. succirubra.* It is lævo-rotatory, but is not fluorescent in its solutions and does not give the thalleioquin reaction.

Cinchonidine Sulphate $(C_{19}H_{22}N_2O)_2H_2SO_4.3H_2O$ (**Cinchonidinæ Sulphas,** U. S. P.).—The official salt is that which crystallizes from a hot and concentrated aqueous solution, while from moderately concentrated aqueous solutions crystallizes a salt with 6 molecules of water. The official sulphate forms silky, acicular crystals, slightly efflorescing on exposure to dry air. It is soluble at 15° in 70 parts of water, and in 1.42 parts of boiling water. It is almost insoluble in chloroform and ether.

Quinoïdine is the name given to the resinous mixture of amorphous alkaloids left in the mother liquor after the extraction of the crystalline bases.

Cinchona barks contain, in addition to the alkaloids, *quinovin*, a non-nitrogenous body of the formula $C_{38}H_{62}O_{11}$, *quinovic acid*, *cinchona-red*, *cinchotannic acid*, and *quinic acid*, together with wax and fat.

3. The Coca Alkaloids.—The leaves of *Erythroxylon coca* and related species contain a number of alkaloids, all of which appear to be derivatives of *ecgonine*, $C_9H_{15}NO_3$. This base is a carboxylic acid of tropine, $C_8H_{15}NO$. When heated with baryta, it splits into carbon dioxide and isotropine. The coca leaves contain some 9 bases, of which the one medicinally important is *cocaine* (benzoyl-ecgonine methyl ester), $C_{17}H_{21}NO_4$. Cocaine may be extracted from the plant, but as separation from the accompanying alkaloids and products of hydrolysis is difficult, Liebermann has proposed a synthetic method which avoids these difficulties and at the same time utilizes the amorphous by-prod-

ucts. The mixed bases are boiled with hydrochloric acid, whereby they all suffer hydrolysis with formation of ecgonine; then by passing dry hydrochloric acid into a solution of ecgonine hydrochloride in methyl alcohol, the hydrochloride of ecgonine methyl-ester is formed, which, on concentrating the alcoholic solution, crystallizes out in prisms. Cocaine is formed when this compound is heated on the water-bath with an equal weight of benzoyl chloride until the mixture becomes homogeneous and the evolution of hydrochloric acid ceases. The melted mass is poured into water and separated from the insoluble benzoic acid, when the cocaine is precipitated by ammonia and recrystallized from alcohol. The artificial alkaloid possesses all the properties of the natural cocaine.

Cocaine crystallizes from alcohol in colorless, monoclinic prisms, melting at 97°–98°. It is very slightly soluble in water, but readily soluble in alcohol, ether, chloroform, benzene, petroleum spirit, and carbon disulphide. Cocaine is lævo-rotatory. Its chief use in medicine is as a local anæsthetic.

Cocaine Hydrochlorate, $C_{17}H_{21}NO_4.HCl$ (**Cocainæ Hydrochloras**, U. S. P.).—It forms colorless, transparent crystals of a saline taste and producing upon the tongue a tingling sensation, followed by a numbness of some minutes' duration. It is readily soluble in water and alcohol, difficultly soluble in ether. At 193° it melts with partial sublimation.

4. The Opium Alkaloids.—Opium contains, besides the two indifferent compounds *meconoisin*, $C_8H_{10}O_2$, and *meconin*, $C_{10}H_{10}O_4$, a series of alkaloids which occur for the most part combined with *meconic acid*. The complete list of the opium alkaloids thus far recognized is:

Morphine, $C_{17}H_{19}NO_3$.
Codeine, $C_{18}H_{21}NO_3$.
Thebaine, $C_{19}H_{21}NO_3$.
Papaverine, $C_{20}H_{21}NO_4$.
Meconidine, $C_{21}H_{23}NO_4$.
Codamine, $C_{20}H_{25}NO_4$.
Laudanine, $C_{20}H_{25}NO_4$.
Laudanosine, $C_{21}H_{27}NO_4$.
Lanthopine, $C_{23}H_{25}NO_4$.
Protopine, $C_{20}H_{19}NO_5$.
Cryptopine, $C_{21}H_{23}NO_5$.
Rhœadine, $C_{21}H_{21}NO_6$.
Narcotine, $C_{22}H_{23}NO_7$.
Oxynarcotine, $C_{22}H_{23}NO_8$.
Narceine, $C_{23}H_{29}NO_9$.
Pseudomorphine, $C_{34}H_{36}N_2O_6$.
Gnoscopine, $C_{34}H_{36}N_2O_{11}$.
Tritopine, $C_{42}H_{54}N_2O_7$.
Hydrocotamine, $C_{12}H_{15}NO_3$.

Of these bases, morphine is always present in opium in largest amount (10 to 14 per cent.). The amount of narcotine present ranges from 4 to 8 per cent., that of papaverine from 0.5 to 1 per

cent., that of codeine from 0.2 to 0.8 per cent., that of thebaine from 0.2 to 0.5 per cent., and that of narceine from 0.1 to 0.4 per cent. The other bases are less important, and are found in relatively small amount. Besides these bases, opium contains some resin and caoutchouc-like bodies, fat, wax, gum, coloring matter, inorganic salts, and water.

Opium, U. S. P., is the concrete, milky exudation obtained by incising the unripe capsules of *Papaver somniferum* Linné (nat. ord. *Papaveraceæ*), yielding in its normal moist condition not less than 9 per cent. of "crystallized morphine," when assayed by the official process (see Part V., Opium Assay). The opium used for pharmaceutical purposes is mainly the Smyrna or Turkey opium, the Persian and East Indian varieties being, however, worked on a large scale for the extraction of alkaloids.

Morphine, $C_{17}H_{19}NO_3 + H_2O$ (**Morphina**, U. S. P.), forms "colorless or white, shining, prismatic crystals or fine needles or a crystalline powder, odorless, and having a bitter taste, permanent in air." It loses its water of crystallization at 120° C. It is difficultly soluble in water, somewhat more soluble in alcohol, insoluble in ether and benzene. Its aqueous solutions are lævo-rotatory.

Morphine when distilled with zinc-dust yields pyridine, quinoline, pyrrol, and phenanthrene. It is considered to be a derivative of a hydrogenized phenanthrene combined with morpholine, $HN<\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}>O$. It contains two OH groups, of which one seems to be phenolic and the other alcoholic in character. In codeine (methyl morphine) the hydrogen of the phenol OH has been replaced, and in methocodeine the hydrogen of the alcoholic OH also.

Color Reactions of Morphine.—A small fragment of a crystal of morphine tested with the following reagents will give color reactions more or less characteristic :

1. With a drop of perfectly neutral solution of ferric chloride or iron-alum is obtained a deep greenish-blue color changed to green by excess of the reagent.

2. Nitric acid (1.42 sp. gr.) will turn the fragment of morphine an orange-red color, which changes to yellow on heating, and is destroyed on adding sodium thiosulphate.

3. Morphine, when pure, yields with pure, concentrated sulphuric acid in the cold either no color or at most a faint pink color. On heating to 150°, a dirty-green (or rose-red) color is developed. On allowing it to cool and diluting with water, a greenish-blue color is produced.

4. The solution of morphine in concentrated sulphuric acid, with a little nitric acid or potassium nitrate added, gives a red coloration turning to brown.

5. Froehde's reagent (pure concentrated sulphuric acid which contains 1 mg. sodium or ammonium molybdate to the c.c.) gives with morphine a fine violet color, changing to blue and dirty green, and ultimately to pale red.

6. A mixture of morphine and cane-sugar (in proportion of 1 to 4) added to concentrated sulphuric acid will give a purple color, changing to blood-red. The addition of a drop of bromine water brings out the color more strongly.

Of the salts of morphine the following are official: **Morphinæ Acetas**, U. S. P., $C_{17}H_{19}NO_3.C_2H_4O_2 + 3H_2O$, **Morphinæ Hydrochloras**, U. S. P., $C_{17}H_{19}NO_3.HCl + 3H_2O$, and **Morphinæ Sulphas**, $(C_{17}H_{19}NO_3)_2H_2SO_4 + 5H_2O$.

When morphine or its hydrochlorate is heated to 140°–150° in a sealed tube with a large excess of strong hydrochloric acid, or with zinc chloride at 110°, it is converted into the hydrochlorate of *apomorphine*, the formula of which differs from that of morphine by the elements of water.

The hydrochlorate (**Apormorphinæ Hydrochloras**, U. S. P.), $C_{17}H_{17}NO_2.HCl$, forms minute grayish-white, acicular crystals, without odor, and of a faintly bitter taste, and acquiring a greenish tint on exposure to air and light. It is moderately soluble in water and alcohol, only slightly soluble in ether or chloroform. Codeine, $C_{18}H_{21}NO_3$, when treated in a similar way with hydrochloric acid, yields first $C_{18}H_{20}ClNO_2$, and then splits off methyl chloride and leaves apomorphine, $C_{17}H_{17}NO_2$.

Codeine is morphine methyl-ester, $C_{17}H_{17}NO(OH)OCH_3$, and has been made synthetically by heating morphine with methyl iodide.

Narceine, $C_{23}H_{29}NO_9$, crystallizes with $2H_2O$ in long, white prisms or needles. The anhydrous base melts, according to Merck, at 170°–171°. It has powerful hypnotic properties.

Narcotine, $C_{22}H_{23}NO_7$, crystallizes from alcohol or ether in colorless needles or prisms, melting at 170°. Above 200° it is decomposed into *meconin*, $C_{10}H_{10}O_4$, and *cotamine*, $C_{12}H_{13}NO_3.H_2O$.

Papaverine, $C_{20}H_{21}NO_4$, is a weak base of feebly narcotic properties.

Thebaine, $C_{19}H_{21}NO_3$.—It crystallizes from strong alcohol in needles, which melt at 193°. It has a sharp and styptic taste, and is a powerful tetanic poison, producing symptoms resembling those of strychnine.

5. The Strychnos Alkaloids.—The various species of *Strychnos* contain certain alkaloids of intensely poisonous properties. Of these two have been specially investigated, strychnine and brucine. Both of them occur in the seeds of the *Strychnos nux vomica* in combination with lactic and igasuric acids, and in the bark of the same. A third base, *igasurine*, supposed to exist in nux vomica, has been shown by Shenstone to be merely a mixture of strychnine and brucine. The seeds of *Strychnos Ignatiæ*, commonly called "St. Ignatius' beans," also contain strychnine and brucine, and are employed for the manufacture of the alkaloids. The decoction of the root-bark of *Strychnos Tieute*, or "deadly upas tree" of Java, evaporated to an extract, is the chief ingredient of the arrow-poison "upas-tieute." It contains strychnine and brucine.

Strychnine, $C_{21}H_{22}N_2O_2$ (**Strychninæ**, U. S. P.).—The alkaloid may be prepared from the several sources above mentioned. The method of its extraction and assay will be given in Vol. II., under Official Assays. Strychnine forms colorless, transparent crystals, odorless, and having an intensely bitter taste perceptible even in very dilute (1 in 700,000) solution. It is difficultly soluble in water, moderately soluble in alcohol, more readily in chloroform, and almost insoluble in ether. Strychnine melts at 268°. Its solutions are lævo-rotatory. It dissolves without color in strong mineral acids. Its solution in strong sulphuric acid, however, is changed by a small fragment of potassium dichromate,* yielding a blue color, changing to purplish-blue, violet, purplish-red, cherry-red, and finally orange-yellow.

Strychnine may be separated from brucine by taking advantage of the insolubility of its ferrocyanide, the corresponding compound of brucine being readily soluble.

Strychnine Sulphate, $(C_{21}H_{22}N_2O_2)_2H_2SO_4.5H_2O$ (**Strychninæ Sulphas**, U. S. P.), forms colorless, prismatic crystals, with an intensely bitter taste, efflorescing in dry air, soluble in water and alcohol, almost insoluble in ether. The salt loses its water of crystallization at 110° and fuses at 200°.

Brucine, $C_{23}H_{26}N_2O_4$.—This second akaloid of *Nux vomica*, *St. Ignatius' beans*, and false angustura bark seems chemically to be a dimethoxy-strychnine. It is obtained in bitter, white crys-

* Allen prefers manganese dioxide as an oxidizing agent for this reaction, as the play of colors is well developed and the change of tints more gradual than with the other oxidizing compounds.

talline powder or groups of prismatic needles. It is more soluble than strychnine in water, and very soluble in alcohol. Brucine is a weaker base than strychnine and is not so poisonous. When treated with concentrated sulphuric acid and oxidizing agents it does not give the color reactions seen with strychnine. On the other hand, with nitric acid of 1.42 sp. gr., brucine gives a blood-red color, which on heating becomes yellowish-red and yellow.

6. Aconite Bases.—*Aconitum napellus* (monk's-hood or wolf's-bane), *Aconitum ferox*, and *A. Fischeri* (Japanese aconite) contain a number of related alkaloids which, according to C. R. Alder Wright, are esters either of benzoic acid or of a derivative of this acid. Thus, when heated with water alone, each of the *crystalline* bases undergoes saponification, with formation of benzoic acid or a derivative thereof, together with a new amorphous base which generally has far less physiological activity than the crystalline alkaloid from which it is derived.

These crystalline alkaloids, together with the products of their hydrolysis, are :

Crystalline Base.	Amorphous Base.	Acid.
Aconitine, $C_{33}H_{45}NO_{12}$ (from *A. napellus*).	Aconine, $C_{26}H_{41}NO_{11}$.	Benzoic acid, $C_7H_6O_2$.
Picraconitine, $C_{31}H_{45}NO_{10}$ (from *A. paniculatum?*).	Picraconine, $C_{24}H_{41}NO_9$.	Benzoic acid, $C_7H_6O_2$.
Japaconitine, $C_{66}H_{88}N_2O_{21}$ (from *A. Fischeri*).	Japaconine, $2C_{26}H_{41}NO_{10}$.	Benzoic acid, $2C_7H_6O_2$.
Pseudaconitine, $C_{36}H_{49}NO_{12}$ (from *A. ferox*).	Pseudaconine, $C_{27}H_{41}NO_9$.	Veratric acid (dimethyl-protocatechuic acid), $C_9H_{10}O_4$.

7. Veratrum Alkaloids.—In the *Veratrum viride* and *V. album* are contained several alkaloids which have been the subject of repeated studies. The most recent views indicate the existence of the following :

Jervine, $C_{12}H_{22}NO_2$.—Melts at 237.7° and is slightly lævorotatory.

Veratroidine (Rubijervine), $C_{32}H_{53}NO_9$.—Melts at 149.2° and is optically inactive.

Pseudojervine, $C_{29}H_{49}NO_{12}$.—Melts at 259.1° and is optically inactive.

Protoveratrine, $C_{32}H_{51}NO_{11}$.—Melts with charring at 245°–250°.

Protoveratridine, $C_{26}H_{45}NO_8$. Melts at 265° ; non-poisonous.

8. Additional Alkaloids.—*Aspidospermine*, $C_{22}H_{30}N_2O$, and *Quebrachine*, $C_{21}H_{26}N_2O_3$, are found, along with other alkaloids, in the bark of *Aspidosperma Quebracho*.

Berberine, $C_{20}H_{17}NO_4 \cdot 5\frac{1}{2}H_2O$, is found in the root of *Berberis vulgaris* and *Hydrastis canadensis*. It forms yellow needles, melting at 120°. When fused with caustic potash it yields quinoline. Associated with it in *Hydrastis canadensis* is the alkaloid *Hydrastine*, $C_{21}H_{21}NO_6$, which forms colorless prisms, melting at 132°, and *Canadine*, $C_{21}H_{21}NO_4$, which forms white, shining crystals, melting at 134°.

Physostigmine, $C_{15}H_{21}N_3O_2$, is found in *Physostigma venenosum* (Calabar bean). It forms colorless or pinkish crystals, only slightly soluble in water, soluble in alcohol and ether. Two of its salts are now official, **Physostigminæ Salicylas**, U. S. P., and **Physostigminæ Sulphas**, U. S. P.

Pilocarpine, $C_{11}H_{16}N_2O_2$, is an alkaloid found in the several varieties of *Pilocarpus*. It is a crystalline alkaloid first found in Jaborandi leaves, but since made synthetically by Hardy and Calmels from β-pyridine-α-lactic acid by first forming pilocarpidine, $C_{10}H_{14}N_2O_2$, and then converting this by the action of methyl iodide into pilocarpine. Two of its salts are official, **Pilocarpinæ Hydrochloras**, U. S. P., and **Pilocarpinæ Nitras**, Br. P.

Piperine, $C_{17}H_{14}NO_3$ (**Piperinum**, U. S. P.), is obtained from the black and white pepper, in which it is found to the amount of from 7 to 9 per cent. It is a weak alkaloidal base, forming pale yellowish crystals, melting at 130°. When heated with alcoholic potash it is decomposed into *Piperidine*, $C_5H_{11}N$, and *Piperic acid*, $C_{12}H_{10}O_4$. The first of these compounds has already been noticed as hexahydropyridine (see p. 798), and the second is related to the oxyacids of the benzene series, and yields piperonal (see p. 770) by its oxidation.

Piperine can be made synthetically by the action of piperidine on the acid chloride, $C_{12}H_9O_3Cl$.

Animal Alkaloids, Ptomaines, and Leucomaines.

While it was pointed out as far back as 1820 that symptoms of poisoning would be developed by introducing into an animal products of decomposing and putrefying organic matter, it has only been since 1870, when the Italian Selmi published his studies on cadaveric poisons, that the subject has been fully appreciated.

He gave the name of "ptomaïnes" to these poisonous products of putrefaction. In 1884, Poehl, of St. Petersburg, in the report of a commission appointed to investigate the subject, stated the following conclusions:

1. Putrefaction, fermentation, and other as yet indefinite alterations of albuminous substances are accompanied by the generation of alkaloid-like bodies,—ptomaïnes.

2. These ptomaïnes may be fixed or volatile, fluid or solid, amorphous or crystalline. They show an alkaline reaction, and form salts with the acids like the alkaloids.

3. Some ptomaïnes are tasteless or odorless; others possess an intense bitter taste or aromatic, sweetish odor. Others, again, evolve a cadaveric odor, or resemble conine or nicotine. They are optically inactive bodies. Their color reactions are as various as those of the vegetal alkaloids, and often simulate them.

Gautier, in 1881, announced the presence of toxic alkaloids in the excretions of animals, and gave to them the name of "leucomaïnes." His explanation of their occurrence is as follows: "While four-fifths of the products of animal combustion are aërobic formations, the remaining part of the combustion of the animal economy takes place at the expense of the tissues and is anaërobic, oxygen taking no part in it. In a normal condition of the body a very small proportion of muscular leucomaïnes is found in urine. But if the air that reaches the blood be diminished in quantity, or if the proportion of hæmoglobin be diminished, as in chlorosis or anæmia, or if substances be introduced into the blood which prevent hæmatosis, substances of the character of leucomaïnes or ptomaïnes accumulate in the blood."

Nitrogenous substances, not alkaloids, which are still poisonous are also formed. These have been named "toxalbumens" or "albumoses."

Among the non-oxygenated liquid ptomaïnes may be enumerated:

Dimethylamine, *Triethylamine*, *Propylamine* (see p. 682). These are monamines.

In the class of diamines (see p. 683) we have: *Putrescine*, $C_4H_{12}N_2$ (tetramethylene-diamine), *Cadaverine*, $C_5H_{14}N_2$ (pentamethylene-diamine). These have both been described on p. 683. Isomeric with the last is *Neuridine*, a non-poisonous ptomaïne from the decomposition of flesh.

Hydrocollidine, $C_{11}H_{13}N$, is a very poisonous ptomaïne found by Gautier in decomposing horse-flesh. *Collidine*, $C_8H_{11}N$ (tri-

methyl-pyridine), and *Parvoline*, $C_9H_{13}N$ (tetramethyl-pyridine), are also found as ptomaïnes.

Tyrotoxicon, $C_6H_5N_2$, found in putrid cheese and in milk and cream after undergoing certain putrefactive changes, also belongs to the non-oxygenated ptomaïnes. It has the composition of the diazo-benzene radical $C_6H_5.N{=}N—$.

Among the more important oxygenated ptomaïnes we may mention :

Neurine, $C_5H_{13}NO$, and *Choline*, $C_5H_{15}NO_2$, are both derived ammonium hydrates, and are described on p. 683. They are both quite poisonous. *Muscarine*, $C_5H_{15}NO_3$, first obtained from the fungus *Agaricus Muscarius*, was found by Brieger in decomposing flesh. *Gadinine*, $C_7H_{16}NO_2$, was found in putrid fish. *Mytilotoxine*, $C_6H_{15}NO_2$, was obtained from poisonous mussels.

CHAPTER IX.

THE TERPENES AND THEIR DERIVATIVES.

I. The Terpenes.

The terpenes are hydrocarbons of the formula $(C_5H_8)_x$. Both they and the camphors, which are oxygenated derivatives, show a close relationship to the aromatic hydrocarbons, as common camphor, $C_{10}H_{16}O$, by the action of certain dehydrating agents yields cymene, $C_{10}H_{14}$, and terpenes of the formula $C_{10}H_{16}$ when heated with iodine are oxidized and yield the same hydrocarbon, $C_{10}H_{14}$. We may therefore consider the terpenes as hydrogen addition compounds of benzene hydrocarbons.*

Characteristic Reactions.—Besides the production of cymene by oxidation, we have other distinctive reactions. The terpenes of the formula $C_{10}H_{16}$ may add on one or two molecules of a haloid acid (HCl, HBr, HI) or the corresponding amount of bromine, showing that they are unsaturated and that their molecules contain either one or two double linkings of carbon atoms. Many terpenes also form characteristic compounds with nitrous acid, called *nitrosites*, such as $C_{10}H_{16}N_2O_3$. These are crystalline compounds, and may be availed of for the separation of many terpenes. Most terpenes also combine with *nitrosyl-chloride*, NOCl, forming *nitrosochloride-terpenes*. These also are crystalline compounds, which combine with organic bases like benzylamine and piperidine to form *nitrolamines*.

Some terpenes form with water crystalline hydrates, as terpin-hydrate, $C_{10}H_{16}(H_2O)_2 + H_2O$. This combination takes place especially in the presence of dilute nitric acid and alcohol. The terpenes frequently polymerize by heating under pressure or by shaking with concentrated sulphuric acid.

Many terpenes are optically active. Frequently a lævo-rotatory and a dextro-rotatory modification of the same terpene may be obtained, which, when mixed, yield an optically inactive variety.

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* A full discussion of the theoretical views held as to the structural formulas of the terpenes and their derivatives by Professor Ed. Kremers, in which Baeyer's proposed system of nomenclature for these compounds is given, will be found in "Proceedings of the American Pharmaceutical Association, 1894."

The terpenes and essential oils have an antiseptic action.

Classification of Terpenes.—Based upon the differences in chemical formulas, as controlled by molecular weight determinations and analysis of derivatives, we may divide the whole class of terpenes into :

1. *Hemiterpenes*, C_5H_8, such as isoprene, which by polymerization yields dipentene, $C_{10}H_{16}$, belonging to the next group.

2. *Terpenes*, $C_{10}H_{16}$. These are the compounds to which in the narrower sense belongs the class name.

3. *Sesquiterpenes*, $C_{15}H_{24}$, include cedrene and cubebene.

4. *Diterpenes*, $C_{20}H_{32}$, include colophene.

5. *Polyterpenes* $(C_{10}H_{16})_x$, include the polymerized hydrocarbons of caoutchouc and gutta-percha.

Based on the formation of the addition compounds before referred to, due to their unsaturated character, we may divide the special terpenes of the formula $C_{10}H_{16}$ into two groups :

1. Such as are able to combine with but one molecule of haloid acid, leaving out of consideration cases of polymerization. This group, which therefore contains only one double linking in the molecule, has been called by Baeyer the *camphane* group. It includes pinene and camphene.

2. Such as are able to combine with two molecules of haloid acid, and therefore contain two double linkings in the molecule. This group has been called the *terpane* group, and includes dipentene, sylvestrene, right and left rotatory limonene, terpinolene, terpinene, and phellandrene.

The characters of these terpenes and their addition compounds may be thus given in tabular form :

Terpene.	Melting Point.	Boiling Point.	Melting Point of Bromides.	Melting Point of Hydrochlorides.	Melting Point of Nitrosites.
Pinene	Liquid	159°–160°	Liquid	$C_{10}H_{16} + HCl$, 125°	
Camphene .	49°	160°–161°	"	$C_{10}H_{16} + HCl$, unstable	
± Limonene . .	Liquid	175°	$C_{10}H_{16}Br_4$, 104°	$C_{10}H_{16} + 2HCl$, 50°	
Dipentene . .	"	175°–176°	$C_{10}H_{16}Br_4$, 125°	$C_{10}H_{16} + 2HCl$, 50°	
Sylvestrene . .	"	175°–176°	$C_{10}H_{16}Br_4$, 135°	$C_{10}H_{16} + 2HCl$, 72°	
Terpinolene .	"	185°–190°	$C_{10}H_{16}Br_4$, 116°	$C_{10}H_{16} + 2HCl$, 50°	
Terpinene . .	"	180°	. . . . .	. . . . .	155°
Phellandrene .	"	170°	. . . . .	. . . . .	94°

Description of the Individual Terpenes.—*Pinene*, $C_{10}H_{16}$, is the chief constituent of the American and French oils of turpentine as well as of juniper oil and eucalyptus oil. Along with

sylvestrene and dipentene it makes up the Russian and Swedish turpentine oils.

Oil of Turpentine (**Oleum Terebinthinæ**, U. S. P.) is distilled from the oleo-resin (crude or virgin turpentine) obtained from *Pinus palustris* (*australis*). The European turpentine is chiefly obtained from *Pinus sylvestris* and *Pinus maritima;* Venice turpentine from *Larix Europæa;* the Strassburg turpentine from *Pinus picea;* Canadian turpentine or Canada balsam from *Abies balsamea.*

The oleo-resin is distilled with steam, whereby the terpenes distil over, leaving as a residue *colophony* resin, which accompanied the essential oil in the original exudation.

The crude oil may be further rectified according to the Pharmacopœial process by distilling with lime water. It then forms a "thin, colorless liquid, of characteristic odor and taste, both of which become stronger and less pleasant by age and exposure to the air." Sp. gr. 0.855 to 0.870. It boils when rectified at 160°. It is almost insoluble in water, easily soluble in alcohol and ether. It dissolves resin, caoutchouc, sulphur, phosphorus, etc. Turpentine oil, like many other mixtures of terpenes, readily absorbs oxygen, and hydrogen dioxide is formed. The oil is then capable of turning guaiacum tincture blue, liberating iodine from potassium iodide, and producing other reactions characteristic of ozone and hydrogen dioxide. Strong nitric acid inflames the oil, but oxidized by dilute nitric acid it yields acids of both the methane series, like butyric, propionic, acetic, and oxalic, and the benzene series like terephthalic and para-toluic. Treated with bromine or iodine it yields cymene.

The American and Russian turpentine oils are right-rotatory, the French, German, and Venetian oils are left-rotatory. These differences are due to the existence of the right and left rotatory varieties of pinene. Inactive pinene may be obtained by heating the pinene nitrosochloride with aniline, whereby NOCl is split off.

Pinene unites with one molecule of HCl to form *Pinene hydrochloride*, $C_{10}H_{17}Cl$, a white solid, melting at 125°, and resembling camphor in appearance and odor, whence the name "artificial camphor." It is insoluble in water, soluble in alcohol. When heated with soaps or weak alkali it splits off hydrochloric acid again and leaves camphene, $C_{10}H_{16}$.

When turpentine oil stands in contact with water, especially in the presence of nitric acid and alcohol, it unites with three molecules of water to form a hydrate, $C_{10}H_{18}(OH)_2 + H_2O$,

known as *Terpin Hydrate* (**Terpini Hydras**, U. S. P.). This is in colorless rhombic prisms of slightly aromatic and somewhat bitter taste, melting at 116°–117°. The anhydrous *terpin*, $C_{10}H_{18}(OH)_2$, obtained in this fusion, or by drying over sulphuric acid, has somewhat of a glycol (or diatomic alcohol) character. When distilled with dilute sulphuric acid it loses a molecule of water and yields *terpineol*, $C_{10}H_{17}(OH)$, an oil of hyacinthine odor which is used in medicine. Still further heating changes it into a mixture of dipentene, terpinene, and terpinolene, all terpenes of the formula $C_{10}H_{16}$.

When sulphuric acid is allowed to stand in contact with oil of turpentine, and the mixture, after a day's standing, is heated to boiling, the oil is changed into an optically inactive mixture of terpenes known as *Terebene* (**Terebenum**, U. S. P.). The Pharmacopœia states that terebene "consists chiefly of pinene, and contains not more than very small proportions of terpinene and dipentene," while Dr. F. B. Power, as the result of a recent research, states that it consists chiefly of the hydrocarbons dipentene and terpinene, with some cymene and camphene. The Pharmacopœia gives the boiling point as 156°–160°, while Dr. Power makes it 170°–185°.

Camphene may be obtained, as already mentioned, by the decomposition of pinene hydrochloride by soap, or with alcoholic potash, also from bornyl chloride, $C_{10}H_{17}Cl$. It exists as dextro- and lævo-camphene. Camphene forms a solid crystalline mass, fusing at 49°, and smelling of turpentine and camphor. It is more stable than pinene, but it is oxidized by chromic acid mixture to common camphor. The addition-compound formed with one molecule of HCl is unstable.

Limonene.—The dextro-limonene, known also as *hesperidene*, *citrene*, or *carvene*, is almost the exclusive constituent of oil of orange-peel, and the chief constituent of oils of dill, caraway, and erigeron. Mixed with pinene it forms lemon oil. It boils at 175°, and forms a tetrabromide, $C_{10}H_{16}Br_4$, fusing at 104°, and dextro-rotatory in character. It is readily changed into inactive limonene or dipentene.

Lævo-limonene is found, according to some authorities, along with lævo-pinene in oil of Norway spruce, although Drs. Bertram and Walbaum, of Schimmel & Co.'s laboratory, state that the limonene of this oil is inactive. The dextro- and lævo-limonene tetrabromides, both fusing at 104°, unite to form a dipentene tetrabromide fusing at 125°.

Dipentene (*Cinene* or *inactive Limonene*) is found in cajuput and camphor oils along with cineol. It is formed from pinene, camphene, limonene, etc., by heating these for several hours to 250°–270°. It is also formed from pinene under the influence of dilute alcoholic sulphuric acid, from terpin hydrate by the splitting off of water, from isoprene by polymerization, from caoutchouc by distillation along with isoprene, and in other ways. It forms a pleasant-smelling liquid with an odor of lemons, boiling at 175°–176°. It readily forms a dihydrochloride and a tetrabromide, both of which have been given in the table (see p. 826). It is more stable than pinene. Its nitrosochloride, by the splitting off of hydrochloric acid, yields a nitrosodipentene, known also as inactive *carvoxine*, fusing at 93°.

Sylvestrene is the dextro-rotatory constituent of Swedish and Russian turpentine oils. It boils at 175°, and is one of the most stable of the terpenes. With acetic anhydride and concentrated sulphuric acid it yields a fine blue color. Its dihydrochloride fuses at 72°, and is dextro-rotatory.

Terpinolene is very similar to dipentene.

Terpinene.—This and the preceding terpene both result from the isomerization of pinene and limonene (see Terpin Hydrate, p. 828). Terpinene forms a nitrosite.

Phellandrene is found in a dextro-rotatory variety in oil of water-fennel, and in a lævo-rotatory variety in oil of *Eucalyptus amygdalina*. It unites readily with nitrous acid to form a solid nitrosite. It is one of the least stable of the terpenes, and readily changes into dipentene, and when treated with alcoholic hydrochloric acid into terpinene.

Sesquiterpenes, $C_{15}H_{24}$.—Hydrocarbons of this formula occur in oils of cubebs and patchouly, and may also be obtained synthetically by the heating of the unsaturated hydrocarbon valerylene, C_5H_8, to 250°–260° under pressure, or by the action of concentrated sulphuric acid upon it. They are all liquid.

Diterpenes, $C_{20}H_{32}$.—Such hydrocarbons are found in copaiba balsam, and are formed by the superheating of turpentine oil. *Colophene*, the residue formed in the manufacture of terebene, is also of this class. It is a thick oil, boiling at 318°.

Polyterpenes, $(C_{10}H_{16})_x$.—These may be obtained by the polymerization of oil of turpentine under the influence of antimony trichloride. They boil at over 250°, and are lævo-rotatory. The terpenes of caoutchouc and gutta-percha probably belong in this class also.

Caoutchouc is the solidified, milky juice of certain tropical trees (*Euphorbiaceæ*, *Asclepiadaceæ*, *Apocynaceæ*). This juice is a vegetable emulsion in which the caoutchouc is suspended in minute globules. This emulsion is coagulated by heat or by the addition of alum and salt solutions. The caoutchouc, at first tough and elastic, on keeping tends to become hard and brittle. To prevent this it is treated with sulphur, the process being known as "vulcanizing." This causes it to retain its elasticity and strength, but it then becomes insoluble in the carbon disulphide, chloroform, and benzene, which dissolve the untreated rubber. When destructively distilled it yields isoprene, C_5H_8, and dipentene, $C_{10}H_{16}$.

Gutta-Percha (from *Isonandra gutta*) is also obtained as a milky juice, which can be coagulated and kneaded into lumps. It forms then a fibrous mass looking like leather clippings cemented together. At ordinary temperatures it is hard and somewhat elastic, but becomes soft when heated. When distilled it yields polyterpenes, but these seem always to be accompanied by oxidation products. It can also be vulcanized by treatment with sulphur.

II. The Camphors.

The camphors are oxygenated derivatives. Of their relationship to cymene and the terpenes mention has already been made. Most of them contain an hydroxyl group, as is shown by their reaction with acids to form esters. They are largely secondary and tertiary alcohols, and like the latter (see Amylene Hydrate), under the influence of dehydrating agents split up into hydrocarbons and water. Carvol, $C_{10}H_{14}O$, and Japan camphor, $C_{10}H_{16}O$, appear, however, to be ketones. Of the camphors the most important are :

Japan Camphor, $C_{10}H_{16}O$ (**Camphora**, U. S. P.), is obtained by distilling with steam the wood of the camphor-tree (*Cinnamomum Camphora*). It may also be obtained synthetically from both borneol and camphene by oxidation.

It forms colorless, translucent, and readily sublimable crystals of a tough consistence, of characteristic odor, melting at 175° and boiling at 204°. It has a crystalline structure, and is readily pulverized in the presence of a little alcohol, ether, or chloroform. It is sparingly soluble in water, but is soluble in alcohol, ether, chloroform, carbon disulphide, benzine, and fixed and volatile oils. It is inflammable and burns with a luminous, smoky

flame. Its sp. gr. is 0.985. The natural camphor is dextro-rotatory ; the artificial camphor is dextro- or lævo-rotatory according to the character of the camphene from which it is prepared. Under the influence of phosphoric oxide it splits off water, yielding cymene. Heated with iodine it yields carvacrol (see p. 760). As camphor combines with both hydroxylamine and phenylhydrazine, it is of ketone character. This is also shown by its relation to the secondary alcohol borneol.

By the action of bromine in proper proportion upon camphor we obtain a bromine substitution compound known as *Monobromated Camphor*, $C_{10}H_{15}BrO$ (**Camphora Monobromata**, U. S. P.). This forms "colorless, prismatic needles, with a mild, camphoraceous odor and taste, permanent in the air, unaffected by light, and neutral to litmus paper." It melts at 76° and sublimes at a slightly higher temperature.

Isomeric with camphor are *pinol*, obtained artificially from pinene, and *absinthol*, contained in oil of wormseed. *Fenchone*, from oil of fennel, *thujone* (*tanacetone*), from oils of thuja root and tansy, and *pulegone*, from oil of pennyroyal, are also ketones of the formula $C_{10}H_{16}O$.

Borneol, $C_{10}H_{18}O$.—Borneol (or Borneo camphor) has been found in the wood of *Dryobalanops aromatica*, and is contained also chiefly in the form of esters in the oils of rosemary, Spanish thyme, valerian, citronella, and the different pine oils. Borneol forms crystals melting at 203°–204° and boiling at 212°, and possessing an odor recalling patchouly and ambergris. When common camphor is reduced by metallic sodium, the product, commercially known as borneol, is a mixture of true borneol and *iso-borneol*. This latter melts at 212°, and has more the odor of tansy and sage. Among the esters of borneol may be mentioned *bornyl acetate*, found in the pine-needle oils, and *bornyl formate* and *bornyl valerianate*, found in oil of valerian.

Isomeric with borneol are *cineol* (*eucalyptol*), found in oils of cajuput, camphor, lavender, rosemary, wormseed, eucalyptus, etc., and *terpineol*, found in oils of cajuput and Japanese valerian, and made synthetically, along with cineol, from terpin.

Isomeric with borneol are also *linalool* and *geraniol*, two monatomic unsaturated alcohols, which either by themselves or through their esters play a very important part in the composition of many of the essential oils.

Linalool, $C_{10}H_{17}OH$, is the essential and fragrant constituent of oil of linaloe, and is found either free or in the form of esters

in oils of lavender, bergamot, petit grains, spike, and coriander. It is a colorless, fragrant liquid of sp. gr. 0.878, and boiling at 197°–198°. It forms a perfectly clear solution with 2 volumes or more of 70-per-cent. alcohol. Its most important esters are *linaloyl acetate* (known as bergamiol and constituting one of the chief constituents of bergamot oil) and *linaloyl formate*.

Geraniol, $C_{10}H_{17}OH$, is the chief constituent of the true geranium oils and of the Turkish geranium or Palmarosa oil. It has also been shown to be the chief constituent of the liquid portion of the oil of rose, and it occurs in addition in oils of citronella, oil of lavender flowers, and one of the eucalyptus oils. It is a colorless liquid with a fragrant rose-like odor, sp. gr. 0.882 to 0.885, and boils at 230°. One part of geraniol requires from 12 to 15 volumes of 50-per-cent. alcohol to form a clear solution. Its most important esters are the *geranyl acetate* and *geranyl formate*.

Both linalool and geraniol when oxidized with chromic acid mixture yield the same aldehyde citral.

Citral, $C_{10}H_{16}O$.—This compound is present to the amount of about 7.5 per cent. in oil of lemon, to which it gives its characteristic odor. It is a golden-yellow liquid of sp. gr. 0.899, and boils at 116° under a pressure of 16 mm., or when perfectly pure at 228°–229° under ordinary pressure without decomposition.

Closely related to citral is another aldehyde-like body, *Citronellal*, $C_{10}H_{18}O$. This is found in oil of *Eucalyptus maculata*, in oil of citronella, and in small amount in oil of lemon. It is a colorless liquid with an agreeable odor, sp. gr. 0.880, and distilling between 205° and 210° with slight decomposition.

Menthol, $C_{10}H_{20}O$ (**Menthol**, U. S. P.), is the most valuable constituent of the several varieties of peppermint oil. It "forms colorless, acicular crystals, having a strong and pure odor of peppermint, and a warm, aromatic taste, followed by a sensation of cold, when air is drawn into the mouth. It melts at 43° C. to a colorless liquid, boils at 212°, and volatilizes slowly at the ordinary temperature. Its alcoholic solution deviates polarized light to the left." Menthol is a secondary alcohol. When oxidized with chromic acid mixture it yields a ketone, *menthone*, $C_{10}H_{18}O$, which also occurs naturally in the peppermint oil. Menthol also forms esters, such as *menthyl formate*, *menthyl acetate*, and *menthyl iso-valerianate*. Of these the latter two are found naturally in the peppermint oil. By the action of dehydrating agents menthol is converted into the hydrocarbon *menthene*, $C_{10}H_{18}$, which boils at 167°

III. The Essential Oils.

By the distillation of the blossoms, flowers, and fruit of many plants with steam are obtained a class of products known as the *essential* or *volatile oils*. They are distinguished both by physical and chemical differences from the *fixed* or *fatty oils*. These latter (see p. 674) are largely mixtures of the glycerin esters of the fatty acids, often containing, in addition, the fat acids in the free state. While the essential oils show some variations in their chemical composition, they are in the main mixtures of terpenes and camphors, although esters of these latter occur, and in a few instances we have aldehydes and ketones.

The fixed oils belong in the aliphatic or methane series of derivatives, while the essential oils all show cyclic or aromatic derivatives among their constituents. The essential oils also show a tendency to absorb oxygen on prolonged exposure to the air and to form resinous products.

Physically the essential oils are characterized by their entire volatility without residue, while the fatty oils are decomposed by heat before volatilization can be completed, and yield acrolein and similar products of decomposition.

The specific gravity of the essential oils is generally less than that of water, and hence they separate on its surface in the product of the steam distillation. They are only very slightly soluble in water, but easily soluble in strong alcohol, chloroform, ether, benzene, and fatty oils. They leave a transient spot only upon paper, while the fixed oils leave a permanent "grease-spot."

The extraction of the essential oils from the plants containing them may be effected:

1. By *distillation*, usually with steam, although in rare cases without. A Florentine receiver is frequently employed to collect the distillate, and by this means the separation of the light, oily layer from the accompanying water is effected.

2. By *expression*. This is followed in cases where the oil is abundant and readily separable, as with oil of lemon, orange peel, etc.

3. By *extraction with solvents*. This solvent may be a liquid fat, as in the case of maceration, a solid fat, as in the case of *enfleurage*, or a volatile solvent, as in the extraction of fine or costly perfumes.

The official essential oils and their proximate chemical composition are as follows:

Oleum Amygdalæ Amaræ, U. S. P. (Oil of Bitter Almond), is a clear, yellowish, thin, and strongly refractive liquid, with a characteristic odor and a bitter, burning taste. Its sp. gr. is from 1.06 to 1.07, and it boils at 180°. It is essentially benzaldehyde, $C_6H_5.COH$, with from 1.5 to 4 per cent. of hydrocyanic acid, and has resulted from the decompostion of the amygdalin of the bitter almond under the influence of the ferment emulsin. (For reaction see p. 766.) Benzaldehyde combines, on standing with hydrocyanic acid, to form the cyanhydrin or nitrile of mandelic acid, $C_6H_5.CH(OH).CN$, a body having the sp. gr. 1.124, and this is, therefore, often contained in oil of bitter almonds.

Oleum Anisi, U. S. P. (Oil of Anise), is "a colorless or pale yellow oil, with characteristic aromatic odor and taste." "At a temperature usually between 10° and 15° it solidifies to a white, crystalline mass." Over 90 per cent. of the oil consists of *anethol* (methoxy-propenyl-benzene) $C_6H_4\begin{cases}OCH_3\\C_3H_5\end{cases}$, the residue containing the isomeric compound *methyl chavicol.*

Oleum Aurantii Corticis, U. S. P. (Oil of Orange Peel), is obtained by expression from the fresh peel of either the Bitter Orange or the Sweet Orange. The chief constituent is the terpene limonene. Oil of sweet orange peel also contains a small amount of *citral* (*geranial*) and a lower boiling aldehyde.

Oleum Aurantii Florum, U. S. P. (Oil of Orange Flowers, or Neroli Oil), is distilled from the fresh flowers of the Bitter Orange. The oil contains, according to Semmler, about 20 per cent. of limonene, 30 per cent. of *nerolol* (a lævo-rotatory alcohol of the composition $C_{10}H_{18}O$, and closely related to linalool), 40 per cent. of *nerolyl acetate*, 3 per cent. of geraniol, and some paraffin.

Oleum Bergamottæ, U. S. P. (Oil of Bergamot).—Obtained by expression from the rind of the fresh fruit of *Citrus Bergamia.* The oil contains limonene, dipentene, linalool, and linaloyl acetate, the last named amounting to from 36 to 39 per cent. Freshly-expressed bergamot oil deposits also *bergapten*, $C_{12}H_8O_4$.

Oleum Betulæ Volatile, U. S. P. (Oil of Sweet Birch), is a colorless or yellowish liquid with a characteristic strongly aromatic odor and taste, closely resembling that of gaultheria or wintergreen. It consists mainly of methyl salicylate (see p. 776), but contains in addition, as established by one of the authors, a small amount (less than 1 per cent.) of a sesquiterpene.

Oleum Cadinum, U. S. P. (Oil of Cade) is a product of the dry distillation of the wood of *Juniperus Oxycedrus.* It is a brownish liquid of a tarry odor and an empyreumatic, burning taste. The oil contains phenols and a sesquiterpene termed *cadinene*, boiling at 274°–275°.

Oleum Cajuputi, U. S. P. (Oil of Cajuput).—A thin, bluish-green liquid (after rectification colorless), with an agreeable camphoraceous odor and an aromatic, bitter taste. It contains cineol (cajuputol), terpineol, terpenyl acetate, and one or more terpenes.

Oleum Cari, U. S. P. (Oil of Caraway), is distilled from the fruit of *Carum Carvi.* The oil contains dextro-rotatory limonene (formerly

known as *carvene*) and dextro-rotatory *carvone*. This body is chemically a ketone of the composition $C_{10}H_{14}O$, and is a liquid boiling at 224°.

Oleum Caryophylli, U. S. P. (Oil of Cloves), is "a pale yellow, thin liquid, becoming darker and thicker by age and exposure to the air, with a strong aromatic odor of cloves, and a pungent and spicy taste." The oil contains *eugenol* (oxy-methoxy-allyl-benzene, $C_6H_3\begin{cases}C_3H_5\\OCH_3\\OH\end{cases}$) to the amount of from 80 to 90 per cent., methyl alcohol, furfurol, and a sesquiterpene termed *caryophyllene*, which boils at 255°. Eugenol, the chief constituent, forms a colorless liquid with the odor and taste of cloves. It has a sp. gr. 1.072, and boils at 253°–254°. It is also found in other essential oils, such as pimenta, bay, Ceylon cinnamon, sassafras, and camphor.

Oleum Chenopodii, U. S. P. (Oil of Chenopodium, or American Wormseed), is a yellowish liquid, with a penetrating odor, and pungent, bitterish taste. It is stated to contain a terpene, $C_{10}H_{16}$, and a body of the formula $C_{10}H_{16}O$.

Oleum Cinnamomi, U. S. P. (Oil of Cinnamon or Oil of Cassia).—"A yellowish or brownish liquid, becoming darker and thicker by age and exposure to the air, with the characteristic odor of cinnamon, and a sweetish, spicy, and burning taste." It consists chiefly of *cinnamic aldehyde*, $C_8H_7.COH$, with some *cinnamyl acetate*, $C_9H_9.C_2H_3O_2$. The amount of cinnamic aldehyde should not be less than 75 per cent.

Oleum Copaibæ, U. S. P. (Oil of Copaiba), is distilled from the so-called Balsam of Copaiba. "It forms a pale yellowish liquid, with the characteristic odor of copaiba, and an aromatic, bitterish, and pungent taste." The oil consists chiefly of *caryophyllene*, $C_{15}H_{24}$.

Oleum Coriandri, U. S. P. (Oil of Coriander), is distilled from the fruit of *Coriandrum sativum*. The oil contains linalool (formerly known as *coriandrol*) and pinene.

Oleum Cubebæ, U. S. P. (Oil of Cubeb), is "a colorless, pale greenish or yellowish liquid, having the characteristic odor of cubeb, and a warm, camphoraceous, aromatic taste." The oil consists chiefly of *cadinene*, $C_{15}H_{24}$, with some dipentene, and when old, or distilled from old fruit, contains *cubeb camphor*, $C_{15}H_{24}.H_2O$.

Oleum Erigerontis, U. S. P. (Oil of Erigeron or Fleabane), is "a pale yellow, limpid liquid, becoming darker and thicker by age and exposure to the air, having a peculiar, aromatic, persistent odor, and an aromatic, slightly pungent taste." It consists chiefly of dextro-rotatory limonene, together with some terpineol.

Oleum Eucalypti, U. S. P. (Oil of Eucalyptus), is "a colorless or slightly yellowish liquid, having a characteristic, aromatic, somewhat camphoraceous odor, and a pungent, spicy, and cooling taste." The oil from the *E. globulus* contains cineol (eucalyptol), dextro-rotatory pinene, small amounts of valeric, butyric, and caproic aldehydes, and ethyl and amyl alcohols. The oil from *E. oleosa* (which is also included as an official source of eucalyptus oil) contains cineol and cuminol. Both of these eucalyptus oils have strongly antiseptic properties due to the cineol (eucalyptol) contained in them.

Oleum Fœniculi, U. S. P. (Oil of Fennel), is distilled from the fruit of *Fœniculum capillaceum*. It contains pinene, phellandrene, dipentene, limonene, *fenchone*, $C_{10}H_{16}O$, and anethol, $C_{10}H_{12}O$, the latter usually in amounts of about 60 per cent. The higher the temperature at which the crystals of anethol separate the better the quality of the oil. Oil of fennel from different sources may differ, and one or more of the above-named constituents may be absent.

Oleum Gaultheriæ, U. S. P. (Oil of Gaultheria or Wintergreen), is distilled from the leaves of *Gaultheria procumbens*. The oil is substantially identical with oil of sweet birch (see p. 834), and consists chiefly of methyl salicylate with a fraction of 1 per cent. of a hydrocarbon, $C_{15}H_{24}$.

Oleum Hedeomæ, U. S. P. (Oil of Hedeoma or American Pennyroyal), distilled from the leaves and tops of *Hedeoma pulegioides*. The oil contains *pulegone*, $C_{10}H_{16}O$, together with two ketones of the formula $C_{10}H_{18}O$ (one being apparently menthone), and formic, acetic, and isoheptoic acids.

Oleum Juniperi, U. S. P. (Oil of Juniper).—It may vary in optical properties, and show either dextro-rotatory, lævo-rotatory, or inactive character. It consists chiefly of pinene, with some cadinene, $C_{15}H_{24}$, and an undetermined substance called *juniper-camphor*, to which the peculiar juniper-like odor and taste are due.

Oleum Lavandulæ Florum (Oil of Lavender Flowers).—The oil contains linalool, linaloyl acetate, geraniol, and a very small amount of cineol.

Oleum Limonis, U. S. P. (Oil of Lemon), is obtained by expression from fresh lemon peel, the rind of the recent fruit of *Citrus Limonum*. It contains a small amount of pinene with dextro-rotatory limonene, about 7 to 8 per cent. of *citral* (see p. 832), and a small amount of citronellal.

Oleum Menthæ Piperitæ, U. S. P. (Oil of Peppermint).—"A colorless, yellowish or greenish-yellow liquid, becoming darker and thicker by age and exposure to the air, having the characteristic strong odor of peppermint, and a strongly aromatic, pungent taste, followed by a sensation of cold when air is drawn into the mouth."

The results of an investigation conducted in the laboratory of Fritsche Bros. at Garfield, N. J., show that the composition of American peppermint oil is quite complex, the following constituents having been noted:

Acetaldehyde.
Amyl alcohol.
Isovaleraldehyde.
Isovalerianic acid.
Dimethyl-sulphide.
Pinene.
Phellandrene.
A lactone, $C_{10}H_{16}O_2$.
Limonene.
Cineol.
Menthone.
Menthol.
Menthyl acetate.
Menthyl isovalerianate.
Cadinene.

Oleum Menthæ Viridis, U. S. P. (Oil of Spearmint), is distilled from the fresh herb of *Mentha viridis*. The oil contains lævo-rotatory carvone and lævo-rotatory limonene, with possibly some lævo-rotatory pinene.

Oleum Myrciæ, U. S. P. (Oil of Myrcia or Oil of Bay), is a yellowish or brownish-yellow liquid, having an aromatic, somewhat clove-like odor, and a pungent, spicy taste. The oil contains the terpenes phellandrene and myrcene, eugenol, methyl eugenol, chavicol, methyl chavicol, and citral.

Oleum Myristicæ, U. S. P. (Oil of Nutmeg), is distilled from nutmeg, the seed of *Myristica fragrans* deprived of its testa. It consists chiefly of pinene, with probably some dipentene, also *myristicol*, $C_{10}H_{16}O$, and *myristicin*, $C_{12}H_{14}O_2$.

Oleum Pimentæ, U. S. P. (Oil of Pimenta or Oil of Allspice).—It is distilled from pimenta, the nearly ripe fruit of *Pimenta officinalis*. The oil contains eugenol and a sesquiterpene, $C_{15}H_{24}$.

Oleum Rosæ, U. S. P. (Oil of Rose), is distilled from the fresh flowers of *Rosa damascena*. Oil of rose when slowly cooled to between 16° and 21° becomes a transparent solid, interspersed with numerous slender scale-like crystals. The liquid fragrant portion of the oil consists for the most part of an alcoholic body of the composition $C_{10}H_{18}O$, which at first was called *rhodinol*, but is now recognized as geraniol (see p. 766). Along with this is some *citronellol*, $C_{10}H_{20}O$. The solid crystallizable portion, or so-called "stearopten," of the oil is odorless when pure, and consists of a mixture of several hydrocarbons, one of which melts at from 35.5° to 36.5°, and has the composition $C_{20}H_{42}$.

Oleum Rosmarini, U. S. P. (Oil of Rosemary), is "a colorless or pale yellow, limpid liquid, having the characteristic, pungent odor of rosemary, and a warm, somewhat camphoraceous taste." The oil contains pinene, cineol, borneol, and camphor.

Oleum Sabinæ, U. S. P. (Oil of Savine), is distilled from the tops of *Juniperus sabinæ*. The oil contains pinene and cadinene, $C_{15}H_{24}$.

Oleum Santali, U. S. P. (Oil of Santal or Sandal-wood), is distilled from the wood of *Santalum album*. The East Indian or official oil of santal contains, according to Chapoteaut, a body called *santalal*, $C_{15}H_{24}O$, boiling at 300°, together with a smaller amount of an alcoholic body, *santalol*, $C_{15}H_{26}O$, which boils at 310°, and is converted by phosphoric oxide into *santalene*, $C_{15}H_{24}$, boiling at 260°.

Oleum Sassafras, U. S. P. (Oil of Sassafras), is distilled from the bark of the root of *Sassafras variifolium*. The oil consists chiefly of *safrol* (methylene ester of allyl-dioxybenzene), $C_6H_3\begin{cases}O\\O\\C_3H_5\end{cases}>CH_2$, a colorless liquid, boiling at from 232° to 233°, together with a very small amount of eugenol, camphor, and the two terpenes pinene and phellandrene.

Oleum Sinapis Volatile, U. S. P. (Volatile Oil of Mustard), is obtained from black mustard, the seed of *Brassica nigra*, by maceration with water and subsequent distillation. It consists chiefly of allyl isosulphocyanate, $CS=N(C_3H_5)$, with traces of carbon disulphide. These products result from the decomposition of the glucoside *sinigrin* (see chapter on Glucosides) under the influence of a naturally occurring ferment myrosin.

Mustard oil is also made artificially by treating allyl iodide with alcoholic solution of potassium sulphocyanate. The resulting allyl-sulpho-

cyanate is changed into the isomeric allyl-isosulphocyanate by heating it to its boiling point. The carbon disulphide seems to be an invariable product of secondary decomposition.

Oleum Terebinthinæ, U. S. P. (Oil of Turpentine), has already been described under Pinene (see p. 827).

Oleum Thymi, U. S. P. (Oil of Thyme), is distilled from the leaves and flowering tops of *Thymus vulgaris*. Its most important constituent is thymol (methyl-propylphenol), $C_6H_3\begin{cases}CH_3\\C_3H_7\\OH\end{cases}$ (see p. 760). In some oils the isomeric compound carvacrol replaces the thymol in whole or part. The oil also contains pinene, cymene, linalool, and small amounts of bornyl esters.

IV. The Resins.

The resins seem to be products of the oxidation of the terpenes. They occur in many essential oils, and seem to form from the hydrocarbons when some of the essential oils are exposed for a time to the air. Unlike the camphors, they are not volatile without decomposition, and, instead of showing the characters of alcohols, aldehydes, and ketones, they are often acids or acid anhydrides.

They may be divided conveniently into at least three groups,—viz., Hard or True Resins, Oleo-resins and Balsams, and Gum-resins.

1. **Hard or True Resins.**—These are solids, fusible but not volatile, and soluble in one or more of the following solvents: alcohol, ether, chloroform, carbon disulphide, fixed oils, volatile oils, fixed alkalies, and ammonia. When soluble in the alkalies it is because of their acid character, and a resin soap is formed. These resins are found either as exudations from plants, when they are generally dissolved in volatile oils, or they may be contained in the cells, ducts, or upon the surface of the plants. Among the hard resins may be enumerated:

Colophonium (Colophony or Common Rosin).—This is obtained from the oleo-resin of the *Coniferæ*, and is the residue when the volatile oil (see *Oleum Terebinthinæ*, p. 827) is distilled off. It forms a yellowish or brown brittle mass, with glossy fracture, melting at about 100°, and soluble in the liquids named above. It is chiefly composed of *abietic anhydride*, $C_{44}H_{62}O_4$, which in the presence of dilute alcohol is converted into abietic acid. Readily saponifiable when mixed with fats, and hence used largely in the manufacture of rosin soaps (see p. 677). Rosin by destructive distillation yields "rosin spirit" and "rosin oil," the

latter of which is used extensively in the manufacture of printer's ink.

Dammar (from *Dammara orientalis* and *D. australis*).—The East Indian dammar is an exudation ; the New Zealand dammar, known also as "Kauri resin," is found fossil as well as of present formation. The resin is harder than colophony ; only partially soluble in alcohol, more soluble in ether, chloroform, and benzene. About 1 per cent. of resin acid only is present. The chief use is for varnishes.

Copal, which is found fossil in Zanzibar and on the West Coast of Africa, is the hardest of these resins, and is especially valuable for the manufacture of varnishes.

Amber (a fossil resin from *Picea succinifera*) is found along the shores of the Baltic and other localities. It melts at 287.5, giving off succinic acid, and at a higher heat, volatile acids and empyreumatic oil of amber.

Lac Resin is an exudation resulting from the puncture of trees by the female insect *Coccus lacca*. The "stick-lac" forms thin branches covered with a brown-red resin ; "seed-lac" is in somewhat rounded fragments detached from the twigs ; "shellac" is the purified resin solidified in thin layers of amber to brown color.

Guaiac Resin is an exudation from the bark of the *Guaiacum officinale*, or melted out of the heart wood by heat. Its alcoholic solution is colored blue on the addition of ferric chloride, chlorine, chromic acid, and other oxidizing agents. The resin fused with caustic potash yields protocatechuic acid. Destructively distilled, it yields guaiacol, creosol (see p. 762), and other products.

Dragon's Blood is a red resin obtained as an exudation from the fruit of *Calamus draco*, growing in Sumatra, Borneo, and adjacent islands. It may contain benzoic and cinnamic acids in small amount. It is used in colored varnishes and various preparations.

Mastic (Mastiche) is obtained as an exudation from incisions in the bark of *Pistacia lentiscus*, and is collected in the island of Scio. It contains from 1 to 2 per cent. of volatile oil, together with two resins. It is used for cements and varnishes.

Sandarac is also obtained as an exudation. Is used chiefly for varnishes of the alcohol or spirit class.

Benzoin (from *Styrax Benzoïn*) is obtained from Sumatra, Java, and Siam. It has an aromatic, acrid taste and an agreeable balsamic odor, and contains from 12 to 20 or 24 per cent. of benzoic acid, cinnamic acid, and several resins, which, fused with

caustic potash, yield para-oxybenzoic acid, protocatechuic acid, and pyrocatechin.

Xanthorrhœa Resin (Acaroid or Botany Bay Resin) is obtained in Australia from *Xanthorrhœa hastilis*. It contains benzoic acid, some cinnamic acid, and resins. Is used in the preparation of varnishes.

2. Oleo-resins and Balsams.—The oleo-resins are mixtures of resins and volatile oils. Those liquid or soft products which contain benzoic and cinnamic acids, in addition to the resin, are generally given the special designation of balsams.

Turpentines (*Terebinthinæ*).—Under this heading may be included the oleo-resins known as common or American turpentine (from *Pinus australis* and *P. tæda*), French or Bordeaux turpentine (from *P. maritima*), Canada balsam (from *Abies balsamea*), Strassburg turpentine (from *Abies pectinata*), Venice turpentine (from *Larix Europœa*), and Russian turpentine (from *Pinus sylvestris* and *P. Ledebourii*). The composition of these several natural mixtures has already been stated under **Oleum Terebinthinæ** (see p. 827).

Burgundy Pitch (**Pix Burgundica**, U. S. P.) and *Canada Pitch* (Hemlock Pitch) are both natural oleo-resins, the former exuding from incisions in the *Abies excelsa*, and the latter from *Tsuga Canadensis*.

Wood Tar (**Pix Liquida**, U. S. P.), on the other hand, is a product of the destructive distillation of the wood of the different species of *Pinus*. It is a very complex mixture, containing pyroligneous acid, acetone, and methyl alcohol, toluene and several of its homologues, naphthalene, pyrene, chrysene, paraffine, phenols, and their esters.

Juniper Tar (see Oil of Cade, p. 834) and *Birch Tar* are similar products of destructive distillation.

Copaiba Balsam (**Copaiba**, U. S. P.) is the oleo-resin of *Copaiba Langsdorfii*, and contains, besides the sesquiterpene *caryophyllene*, resins, of which one, *copaivic acid*, $C_{20}H_{30}O_2$, is crystalline.

Elemi is an oleo-resin exuding from incisions in *Canarium commune*, in the Philippine Islands. It contains, besides volatile oil, a mixture of resins (breïn, amyrin, bryoïden, breïdin, and elemic acid).

Gurjun Balsam (Wood Oil) is a liquid exudation from the species of *Dipterocarpus*, and contains volatile oil, said to be identical with oil of copaiba, and resin.

Peru Balsam (**Balsamum Peruvianum**, U. S. P.) is of a syrupy consistence and reddish-brown color, with a balsamic and smoky odor. The oily liquid which separates on agitation with

caustic potash, called cinnamein, is made up of benzyl alcohol, benzyl benzoate, and benzyl cinnamate. The resin, which is admixed with the oil, yields by dry distillation benzoic and cinnamic acids, styrene, and toluene, together with styracine (cinnamyl cinnamate).

Tolu Balsam (**Balsamum Tolutanum**, U. S. P.) is a balsam obtained from *Toluifera Balsamum*, a tree growing in Venezuela and New Grenada.

The balsam is at first semi-solid, but becomes harder by age. It contains benzyl benzoate and cinnamate, free benzoic and cinnamic acids, *tolene*, $C_{10}H_{16}$, and two resins, which make up over 80 per cent. of the balsam.

Liquidambar (Sweet Gum) is an exudation from *Liquidambar styraciflua*. It is a thick brownish-yellow liquid or solid resin. It contains a mixture of cinnamic esters, the hydrocarbon styrol (or cinnamene), C_8H_8, and two resins known as α-storesin and β-storesin.

Storax (**Styrax**, U. S. P.) is a balsam obtained from *Liquidambar orientalis*. The principal constituent is *storesin*, $C_{36}H_{55}(OH)_3$, and its cinnamic ester. Several other esters of cinnamic acid, a little vanillin, and styrol or cinnamene are the other constituents.

3. Gum-resins.—These are milky exudations from plants, and contain gum which is wholly or partly soluble in water and resin soluble in alcohol. Many gum-resins also contain essential oil. Of this class are *Asafetida* (**Asafœtida**, U. S. P.). It is a gum-resin obtained from the root of *Ferula fœtida*. It contains from 3 to 9 per cent. of volatile oil (containing sulphur), 20 to 30 per cent. of gum, and 50 to 70 per cent. of resin. This latter contains a little ferulaic acid (see p. 781), on dry distillation yields umbelliferon, and fused with caustic potash gives resorcin and protocatechuic acid.

Galbanum is a gum-resin brought from Persia. It contains from 6 to 9 per cent. of volatile oil, gum, and from 60 to 66 per cent. of resin. This latter also yields umbelliferon, $C_9H_6O_3$, on distillation, and resorcin on fusion with caustic potash.

Sagapenum is a very closely-related gum-resin.

Ammoniac (**Ammoniacum**, U. S. P.).—A gum-resin obtained from *Dorema ammoniacum*. It contains volatile oil (free from sulphur), gum, and resin. It does not yield umbelliferon on distillation, but does yield resorcin and protocatechuic acid on fusion with caustic potash.

Olibanum (or Frankincense) is a gum-resin exuding from the several species of *Boswellia* in Eastern Africa and Southern Arabia. It contains from 4 to 7 per cent. of essential oil, from 56 to 72 per cent. of resin, and about 30 per cent. of gum. When burned it develops a strongly aromatic odor.

Myrrh (**Myrrha**, U. S. P.) is a gum-resin exuding from the *Commiphora Myrrha* in Eastern Africa and Southwestern Arabia. It contains from 2 to 4 per cent. of volatile oil, from 25 to 40 per cent. of resin, and from 40 to 60 per cent. of gum. Fused with caustic potash the resin yields pyrocatechin and protocatechuic acid. It is used extensively in the form of tincture and powders.

Bdellium is a gum-resin very similar in character to myrrh.

Gamboge (**Cambogia**, U. S. P.) is a gum-resin exuding as a milky juice from incisions in *Garcinia Hanburii*, and is collected in bamboo joints, and comes into commerce in cylindrical pieces. It forms a yellow emulsion with water. It contains 16 to 26 per cent. of gum, 66 to 80 per cent. of resin or *cambogic acid*, and about 4 per cent. of wax.

Euphorbium is an exudation from incisions in the stem of the *Euphorbia resinifera* from Morocco. It contains 18 per cent. of gum, 38 per cent. of resin, some starch, malates, and ash.

Scammony (**Scammonium**, U. S. P.) is a milky juice collected in Western Asia from the *Convolvulus Scammonia*. It forms a greenish emulsion with water. It contains from 75 to 90 per cent. of resin, known as *scammonin*, $C_{34}H_{56}O_{16}$, identical with the *orizabin* of *Ipomea orizabensis*, and converted by alkalies into scammonic acid, which is soluble in water. The rest of the drug is gum, soluble in water.

Tschirch has recently proposed a new classification of the resins. He divides them into :

I. *Resin esters*, including (*a*) *resinoles*, or resin-alcohols, and (*b*) *resinotannoles*, which latter are colored and give the tannin reaction.

II. *Resin acids* (resinol acids). These are oxy acids,—that is, contain both the carboxyl and hydroxyl groups.

III. *Resenes* (indifferent bodies of unknown origin belonging to the aromatic series).

CHAPTER X.

GLUCOSIDES—BITTER AND NEUTRAL PRINCIPLES.

I. Glucosides.

Under this name have been grouped a number of compounds, occurring mainly in the vegetable kingdom, that under the influence of dilute acids or ferments are split up into component parts, of which glucose or a related carbohydrate always is one. The glucosides appear to be, not esters, but ethers, which, under the treatment above referred to, take up the elements of water, and then yield the glucose and other products.

While sharing this method of decomposition in common they show in other respects a wide divergence. Thus, solanin is a nitrogenous base, and is thus at once an alkaloid and a glucoside, while other glucosides, like myronic acid, are of well-defined acid character. The most of the glucosides, however, are neutral bodies, although they frequently combine with metallic oxides, such as lead and mercuric oxides. They are usually soluble in water and in alcohol, often insoluble in ether, and generally crystallizable. On heating with concentrated sulphuric acid and the bile acids, the glucosides give, like the sugars, the Pettenkofer bile reaction,—viz., a deep-red color. Alkaline copper solution is reduced by most, but not all, of the glucosides. Ammoniacal silver solution is reduced by glucosides, as by cane-sugar and mannite, only after the addition of caustic alkali. Many glucosides are optically active, most of them showing a lævo-rotatory character. This rotatory power does not, however, correspond in any way to that of the sugar, which is obtained by the decomposition of the glucoside.

Glucosides, as a rule, are not decomposed by pure water, even on boiling or heating under pressure, but dilute acids readily effect the decomposition, sulphuric and hydrochloric being chiefly used. Alkalies may also effect the decomposition, although baryta water is better adapted, as the stronger alkali generally acts upon the sugar liberated, decomposing or altering it. The splitting up of the glucosides is, however, often best effected by the action of ferments, which may act at the ordinary or only slightly elevated temperature. Among such ferments may be

mentioned *emulsin*, an albuminoid found in the almond ; *myrosin*, found in mustard-seed ; and the ferment contained in the saliva.

For the extraction of glucosides from the plant it frequently suffices to extract with water or alcohol, and to crystallize the glucoside from the concentrated extracts after decolorizing with animal charcoal ; or, after defecating the decoction from the plant with neutral acetate of lead, which does not affect the glucoside as a rule, the addition of basic lead acetate will precipitate it in the form of a weak combination readily decomposed by hydrogen sulphide. Tanret has proposed still another procedure. After leaving the finely-pulverized plant material in contact with milk of lime for 24 hours, he extracts with distilled water in a displacement apparatus, and precipitates these extraction liquors with a concentrated solution of sodium chloride ; the precipitate is dried, preferably in vacuo, and extracted with chloroform, which dissolves the glucoside, which can then be crystallized out.

The first successful synthesis of a natural glucoside was accomplished by Arthur Michael in 1879, who caused acetochlorhydrose (obtained by the action of acetyl chloride upon glucose) to act upon the potassium compound of salicyl-aldehyde in alcoholic solution, when helicin was formed, and this, by the action of sodium amalgam, was converted into salicin. The same synthesis led to the formation of populin (benzoyl-salicin), and the corresponding reaction of acetochlorhydrose upon the potassium compound of methyl-hydroquinone led to the synthesis of methyl-arbutin, another naturally occurring glucoside. A newer and much more generally applicable method for the synthesis of the glucosides has been recently announced* by Emil Fischer. He finds when glucose and other sugars of the monosaccharide class (see p. 686) are dissolved in an alcohol, and hydrochloric acid gas is passed in, there forms a glucoside or mixed ether with the elimination of water. This reaction seems to be available for all the alcohols ; in the case of glucose it has been proved with methyl, ethyl, propyl, isopropyl, amyl, allyl, and benzyl alcohols, as also with ethylene glycol and glycerin. It may even be employed for the hydroxy-acids (alcohol-acids), as was proved by the preparation of lactic glucoside. Where the sugar is completely insoluble in the alcohol, which is the case with many compounds of the aromatic and terpene series, in place of glu-

*Berichte der Chem. Ges., 1893, p. 2400.

cose, acetochlorhydrose, or pentacetyl-glucose, may be employed, as both are soluble in ether, benzene, and chloroform. As the bioses (cane- and milk-sugar and maltose) are hydrolyzed by hydrochloric acid, they cannot be converted in this way into glucoside-like compounds. These new artificial glucosides, like the natural ones, are unattacked by boiling alkalies, Fehling's solution and phenyl-hydrazine ; if, however, they be heated with dilute acids they are readily hydrolyzed into their components. They are likewise hydrolyzed by the invertase of yeast.

The glucosides which are of more especial pharmaceutical or medical importance are the following :

Amygdalin, $C_{20}H_{27}NO_{11}.3H_2O$, is found in bitter almonds and in the kernels of fruit. It is extracted by alcohol from the compacted cake of the almond after the oil has been pressed out. It forms a white, crystalline powder, of slightly bitter taste, melting at 200°. When boiled with dilute acids, or when the aqueous extract of the bitter almond is digested at 25°–35°, it is decomposed according to the reaction :

$$C_{20}H_{27}NO_{11} + 2H_2O = C_7H_6O + CNH + 2C_6H_{12}O_6,$$

the products being benzaldehyde, hydrocyanic acid, and dextrose. In the latter case the decomposition is brought about by the *emulsin*, or soluble ferment, which occurs in both the sweet and the bitter almond.

Æsculin, $C_{15}H_{16}O_9.1\frac{1}{2}H_2O$, is found in the bark of the horse-chestnut. It forms prisms of a bitter taste, melting at 160°, and is decomposed by boiling with dilute acids or by emulsin into *glucose* and *æsculetin* (dioxycoumarin) :

$$C_{15}H_{16}O_9 + H_2O = C_6H_{12}O_6 + C_9H_6O_4.$$

Arbutin, $C_{12}H_{16}O_7.\frac{1}{2}H_2O$, and *Methyl-arbutin*, $C_{13}H_{18}O_7$, are contained in *Arbutus Uva-ursi* and *Chimaphila umbellata* and other ericaceous plants. Both are bitter, crystallizable principles, separable only with difficulty. Both are decomposed by dilute acids or emulsin, the former into glucose and hydroquinone, and the latter into glucose and methyl-hydroquinone.

Carminic Acid, $C_{17}H_{18}O_{10}$, is the coloring constituent of cochineal (the dried female insect *Coccus cacti*), and the essential constituent of the commercial "carmine," obtained by extracting the cochineal with water and precipitating with alum. It is an amorphous, purplish-red mass, soluble in water and alcohol, which on boiling with dilute acids is decomposed as follows :

$$C_{17}H_{18}O_{10} + 2H_2O = \underset{\text{Carmine-red.}}{C_{11}H_{12}O_7} + \underset{\text{Carmine-sugar.}}{C_6H_{10}O_5}.$$

Cerebrin is a nitrogenous glucoside contained in brain- and nerve-tissue. On boiling with dilute sulphuric acid it yields galactose (cerebrose).

Chitin, $C_{15}H_{26}N_2O_{10}$, is another animal glucoside found in the outer shells of the *Crustaceæ*. It is an amorphous substance, which when boiled with strong hydrochloric acid is decomposed into *acetic acid* and *glycosamine*, $C_6H_{11}O_5.NH_2$.

Coniferin, $C_{16}H_{22}O_8.2H_2O$, is a glucoside found in the cambial juice of the *Coniferæ* and in the woody tissue of the sugar-cane. It is decomposed by emulsin into *glucose* and *coniferyl-alcohol*, according to the reaction :

$$C_{16}H_{22}O_8 + H_2O = C_{10}H_{12}O_3 + C_6H_{12}O_6.$$

When oxidized with chromic acid mixture coniferin yields vanillin (see p. 770). On the other hand, if oxidized by weaker agents, like potassium permanganate, the coniferin is changed into *gluco-vanillic acid*, $C_{14}H_{18}O_9$, and *gluco-vanillin*, $C_{14}H_{18}O_8$. By the action of emulsin or dilute mineral acids, these artificial glucosides are split up into glucose and vanillic acid, or vanillin, as the case may be.

Convolvulin, $C_{34}H_{56}O_{16}$, and *Jalapin*, $C_{31}H_{50}O_{16}$, are two glucosides contained in jalap resin, the former chiefly obtained from *Ipomœa orizabensis* (Mexican male jalap), and the latter from *Ipomœa Jalapa*. When jalap resin is boiled with dilute sulphuric acid some time and filtered, we obtain a mixture of *jalapinol*, $C_{13}H_{24}O_3$, and *convolvulinol*, $C_{16}H_{30}O_3$.

Digitalin.—The leaves of the foxglove (*Digitalis purpurea*) yield several medicinally active principles which are glucosides, but the true composition of which seems still to be a matter of controversy.

The French or crystalline preparation, difficultly soluble in alcohol, seems to consist chiefly of *digitoxin*, $C_{21}H_{32}O_7$, which is not a glucoside. On the other hand, the German preparation is amorphous and easily soluble in alcohol. It contains *digitonin*, $C_{31}H_{52}O_{17}$, *digitalein*, $C_{22}H_{38}O_9$, and *digitalin*, $(C_5H_8O_2)_n$. The first of these breaks up on boiling with dilute acids into sugar and two compounds, *digitoresin* and *digitonein ;* the second and the third both break up into glucose and *digitaliresin*.

Frangulin, $C_{21}H_{20}O_{10}$, is a glucoside found in the bark of *Rhamnus frangula*. It is decomposed on hydrolysis into rhamnose, $C_6H_{12}O_5$, and *emodin* (trioxymethyl-anthraquinone), $C_{15}H_{10}O_5$.

Glycyrrhizin, $C_{44}H_{63}NO_{18}$, is found in liquorice-root (*Glycyrrhiza glabra*) as the acid ammonium salt, $C_{44}H_{62}(NH_4)NO_{18}$.

The salt is obtained in yellowish scales, the free glycyrrhizic acid in a gelatinous mass. It is decomposed on boiling with acids into *glycyrrhetin*, $C_{32}H_{47}NO_4$, and *parasaccharic acid*, $C_6H_{10}O_8$.

Helicin, $C_{13}H_{16}O_7$, is an oxidation product of salicin. It is split up by the action of dilute acids or emulsin into salicylic aldehyde, $C_6H_4\begin{cases}OH\\COH'\end{cases}$ and dextrose, $C_6H_{12}O_6$. Its synthesis by Michael has already been described.

Helleborin, $C_{36}H_{42}O_6$, and *Helleborein*, $C_{26}H_{44}O_{15}$, are glucosides occurring in the roots of black hellebore (*Helleborus niger*) and green hellebore (*H. viridis*).

Indican, $C_{26}H_{31}NO_{17}$, is a glucoside found in woad (*Isatis tinctoria*). It is decomposed by heating with dilute acids into *indiglucin*, $C_6H_{10}O_6$, and indigo-blue, C_8H_5NO. The reaction, however, is not a complete one, as other side-products are obtained. The so-called "indican" found in the urine at times is indoxylsulphuric acid (see p. 786).

Myronic Acid, $C_{10}H_{19}NS_2O_{10}$, is found in black mustard-seed as the potassium salt. The free acid is unstable. The potassium salt is decomposed by a ferment, *myrosin*, which is found mainly in the white mustard-seeds, according to the reaction:

$$C_{10}H_{18}NS_2O_{10}K = C_6H_{12}O_6 + KHSO_4 + C_3H_5.NCS,$$

the products being dextrose, acid potassium sulphate, and allyl-sulphocyanate (mustard oil).

Phloridzin, $C_{21}H_{24}O_{10}.2H_2O$, is a glucoside found in the root-bark of the apple-, pear-, plum-, and cherry-tree. It forms silky needles, fusing at 106°–108°. It is decomposed by dilute acids into glucose and *phloretin*, $C_{15}H_{14}O_5$. This latter decomposition product appears to occur also ready formed in the root-bark of the apple-tree.

Populin, $C_{20}H_{22}O_8$ or $C_{13}H_{17}(C_6H_5CO)O_7$, is benzoyl-salicin, and is found along with salicin in the bark and leaves of *Populus tremula*. When heated with dilute mineral acids it is split into glucose, benzoic acid, and saligenin. It is made synthetically from salicin by treatment with benzoyl-chloride.

Quercitrin, $C_{36}H_{38}O_{20}.3H_2O$, is a glucoside contained as the coloring principle of quercitron bark (from *Quercus tinctoria*). When boiled with dilute acids it splits up into *quercetin*, $C_{24}H_{16}O_{11}$, and *isodulcite*, $C_6H_{14}O_6$.

Ruberythric Acid, $C_{26}H_{28}O_{14}$, is the constituent of the madder-root, which by its decomposition yields alizarine, the reaction being:

$$C_{26}H_{28}O_{14} + 2H_2O = C_{14}H_8O_4 + 2C_6H_{12}O_6.$$

The purpurine of madder-root appears also to be a decomposition product of another glucoside occurring naturally in the root.

Salicin, $C_{13}H_{18}O_7$, is the glucoside of the willow-bark, and is contained as well in the young twigs and the leaves of the tree. It is also contained in the poplar and in castoreum. Its artificial production from helicin has already been mentioned. When heated with dilute acids, or treated with emulsin, it is decomposed into dextrose and *saligenin* (*o*-oxybenzyl alcohol, $C_6H_4\left\{\begin{matrix}OH\\CH_2OH\end{matrix}\right)$.

Saponin (Senegin), $C_{19}H_{30}O_{10}$, is found in many plants, as *Saponaria officinalis*, **Senega**, U. S. P., **Quillaja**, U. S. P., and others. It forms a powder, which dissolves in water to form a frothy liquid. On boiling with water it is decomposed into glucose and *sapogenin*, $C_{14}H_{22}O_2$, which crystallizes and is insoluble in water.

Sinalbin, $C_{30}H_{44}N_2S_2O_{16}$, is a glucoside found in the white mustard-seed. It is decomposed by the ferment myrosin found in the same seeds into glucose, sinalbin-sulphocyanate (or sinalbin-mustard oil), $C_7H_7O.NCS$, and acid sulphate of sinapin, $C_{16}H_{24}NO_5.HSO_4$.

Solanin, $C_{42}H_{75}NO_{15}$, is a poisonous alkaloid-like glucoside found in the Solanum species and in potato-sprouts. It forms crystalline needles, melting at 235°. It is decomposed by dilute acids into dextrose and solanidin, $C_{26}H_{41}NO_2$.

Xanthorhamnin (Rhamnin), $C_{48}H_{66}O_{29}$, is the coloring matter of *Rhamnus infectoria* and *R. tinctoria*, and of the so-called Persian berries from the same. On heating with dilute acids the glucoside is decomposed into *isodulcite*, $C_6H_{14}O_6$, and *rhamnetin*, $C_{12}H_{10}O_5$.

II. Bitter Principles and Neutral Bodies.

In this class we include a number of bitter principles, sometimes crystallizable, sometimes resinous, the chemical nature of which is not as yet sufficiently settled to allow of their classification under the proper heads, and some vegetable coloring principles found in the natural dyewoods which are equally undetermined as to their chemical relationship. The more important will be enumerated in alphabetical order.

Alkannin, $C_{15}H_{14}O_4$, is contained in alkanna root (*Anchusa tinctoria*). It forms a brownish-red mass, which dissolves in alkalies with blue color. Distilled with zinc-dust it yields methyl-anthracene.

Aloin, $C_{17}H_{18}O_7.\frac{1}{2}H_2O$, is the active constituent of aloës. It crystallizes in yellowish needles and has a bitter taste. Dis-

tilled with zinc-dust it yields anthracene. The benzene solution of aloin, when heated with ammonia, gives a violet-red color.

Bixin, $C_{28}H_{34}O_5$, is obtained from "orlean," the fruit of *Bixa orellana*. It forms reddish scales melting at 175°–176°. It is still extensively used in dyeing, as it colors animal and vegetable fibres yellow without the aid of mordants. It is also well known under the name of "annatto" in its use in butter color and the coloring of cheese.

Brasilin, $C_{16}H_{14}O_5$, is obtained from Brazil wood (*Peltophorum dubium*). It forms amber-yellow crystals, which dissolve in alkalies with carmine color. When fused with potassium hydrate it yields resorcin. It is also used extensively in dyeing on wool and cotton.

Cantharidin, $C_{10}H_{12}O_4$, is found in Spanish flies (*Lytta vesicatoria*). It forms tablets melting at 218°. When heated with phosphorus pentasulphide it yields *o*-xylol. When cantharidin is heated with alkalies it takes up the elements of water and forms *cantharidic acid*, $C_{10}H_{14}O_5$, an unstable acid, the potassium salt of which is used in medicine.

Chlorophyll is the name given to the green coloring matter of fresh vegetation. It appears to be a mixture of a yellow coloring matter, *xanthophyll*, and a blue coloring matter, *cyanophyll*. A crystalline product is also obtained, *chlorophyllan*, which by reduction with zinc-dust yields the original chlorophyll.

Cotoïn, $C_{22}H_{18}O_6$, is obtained from the coto bark of Bolivia. Forms pale-yellow crystals melting at 130°. When fused with caustic potash or heated with concentrated hydrochloric acid to 140°, benzoic acid is split off.

Cubebin, $C_{10}H_{10}O_3$, is obtained from cubeb, the unripe fruit of *Piper Cubeba*. It forms small needles melting at 125°. When oxidized by nitric acid it yields oxalic and picric acids; when fused with caustic potash it yields acetic and protocatechuic acids.

Curcumin, $C_{14}H_{14}O_4$, is the coloring principle of the turmeric root (*Curcuma tinctoria*). It forms yellow prisms melting at 178°. It is changed to a reddish-brown by alkalies, whence its use as an indicator for alkalies. It is used somewhat for dyeing in compound colors.

Biliary Pigments.—In the bile and biliary calculi are found several pigments of definite composition. The best known are *bilirubin*, $C_{16}H_{18}N_2O_3$; *biliverdin*, $C_{16}H_{18}N_2O_4$; *bilifuscin*, $C_{16}H_{20}N_2O_4$; and *biliprasin*, $C_{16}H_{22}N_2O_6$. These biliary pigments may be recognized by Gmelin's test, in which nitric acid containing nitrous acid is added, when colors changing from

green to bluish, violet, red, and yellowish-red are produced. Bilirubin forms an insoluble calcium compound which is found in biliary calculi.

Hæmatoxylin, $C_{16}H_{14}O_6 \cdot 3H_2O$, is the coloring principle of logwood (*Hæmatoxylon campechianum*). It forms colorless crystals, turning red on exposure to light. Its solution is dextro-rotatory, and reduces Fehling's solution; it is dissolved by ammonia solution with a purplish color. This solution absorbs oxygen from the air, and then deposits *hæmateïn*, $C_{16}H_{12}O_6$. Logwood and its extracts are used extensively in dyeing and calico-printing and other applications.

Litmus, as well as *Orseille* (or Archil), results from the fermentation of colorless compounds contained in certain lichens. The coloring matter of litmus appears to be *azolitmin*, $C_7H_7NO_4$, while that of orseille extract is *orceïn*, $C_7H_7NO_3$. Litmus acts like a weak acid, the salts of which are blue (the potassium compound existing in the commercial litmus), and which, when set free by acids, is reddish in color. Hence the use of litmus as an indicator.

Picrotoxin, $C_{30}H_{34}O_{13}$, is contained in the seed of *Anamirta paniculata*. It crystallizes in needles melting at 201°; is very bitter and poisonous.

Protagon, $C_{160}H_{308}N_5PO_{35}$, is found in the brain. It is soluble in warm alcohol, from which it separates on cooling in fine crystals. It is decomposed on boiling with baryta water into *cerebrin* (see p. 846) and the decomposition products of *lecithin* (*neurin* (see p. 683), *glycerin*, *phosphoric acid*, and *fatty acids*).

Quassin, $C_{32}H_{42}O_{10}$, is the bitter principle of quassia-wood (*Picræna excelsa*). It forms colorless leaflets, with an extremely bitter taste. Its aqueous solution reduces Fehling's solution, and is precipitated by tannin.

Santalin, $C_{15}H_{14}O_5$, is the coloring principle of Red Saunders, from *Pterocarpus santalinus*. It forms reddish prisms melting at 104°. Soluble in alcohol with blood-red color, in alkalies with violet color. It is used along with the related woods (barwood and cam-wood) in dyeing.

Santonin, $C_{15}H_{18}O_3$ (**Santoninum**, U. S. P.), is the active principle of wormseed (*Artemisia pauciflora*). It forms colorless prismatic crystals fusing at 170°. It is the anhydride of *santonic acid*, $C_{15}H_{20}O_4$, into which it is readily converted by bases.

CHAPTER XI.

TISSUE-FORMING SUBSTANCES, OR PROTEID MATTER.

WHILE it was stated in the beginning of our discussion of organic compounds (see p. 587) that the distinction between *organic* bodies (those produced in connection with the processes of life) and *inorganic* bodies (those found in the mineral kingdom or formed from mineral matter) no longer existed, no mention was made of *organized* tissue. The living plant or animal, no matter how elementary its structure, is largely composed of cells, of which the invariable organic constituents are proteids. In plant tissue the proteids share their importance with cellulose and its alteration products, but in the animal tissue they are so fundamentally important that it has well been said "that they are indispensable constituents of every living, active, animal tissue, and indissolubly connected with every manifestation of animal activity."

The proteids of the animal body all come, directly or indirectly, from vegetable sources, the nitrogenous or proteid principles of which form an important element in our food. By the action of certain ferments present in the alimentary juices (p. 704) all proteids are capable of being converted into closely-allied bodies called peptones, which, after absorption, are capable of reconversion into proteids. Not all the proteids of the food are so reconverted, however, or go to the building up of wasting proteid tissues and organs; much undergoes decomposition, producing carbon dioxide, water, and simpler nitrogen compounds like urea, $CO(NH_2)_2$.

The various proteids are highly complex compounds of very high molecular weight and unknown constitution, containing carbon, hydrogen, oxygen, nitrogen, and sulphur, and in some cases phosphorus and iron, in percentage composition ranging within the following limits:

	C.	H.	N.	S.	O.	P.
From	50.6 per cent	6.9	15.2	0.3	20.9	0.00
to	54.5 "	7.3	17.6	2.2	23.5	0.85

In addition to these constituents, the proteids, no matter how carefully purified, usually leave when ignited a small quantity of

mineral matter, composed chiefly of alkaline chlorides and phosphates.

All of the proteids are optically active, and their solutions are all lævo-rotatory in varying degree.

Only certain of the proteids are soluble in water; they are all soluble, however, especially with the aid of heat, in concentrated acetic acid, and in solutions of the alkali hydrates; they are insoluble in cold absolute alcohol and in ether.

CHEMICAL REACTIONS OF THE PROTEIDS.

I. Precipitation Reactions.

Slightly acid (especially acetic acid) albumen solutions are *coagulated* on heating, and this change is hastened by the presence of salts such as sodium chloride. The temperature of coagulation differs for the different proteids, and hence can be used for their identification and separation. On addition of *dilute nitric acid* most proteids give a precipitate of yellow *xanthoproteic acid;* peptones, however, do not give the reactions. *Potassium ferrocyanide* in the presence of an excess of dilute acetic acid precipitates proteids. From acetic acid solution proteids are also precipitated by adding *sodium chloride* and neutral salts of the alkalies to saturation. *Trichloracetic acid* will precipitate most proteids quantitatively from solution; peptones, however, constitute an exception. Most of the *alkaloidal precipitants* (see p. 804) will also precipitate proteid compounds.

II. Color Reactions.

The albuminoids, if present, cause the solution to take a yellow color on addition of *concentrated nitric acid*, constituting the "xanthoproteic reaction." *Millon's reagent*,* added to a solution containing even a trace of a proteid, and the mixture heated, causes a purple-red coloration. A mixture of 1 volume of concentrated sulphuric acid and 2 volumes of glacial acetic acid, when heated, causes proteids to assume a violet-red color. Glue, however, does not show this change. This is known as "Adamkiewicz's reaction." Many proteids, treated with sodium hydrate and a few drops of copper-sulphate solution, show in the cold a reddish-violet color. This develops most readily with

* Millon's reagent is made by dissolving 1 part by weight of mercury in 2 parts of nitric acid of specific gravity 1.42, and, after complete solution, diluting each volume of the liquid with two volumes of water.

peptones; with other proteids heat must be applied. It is known as the "Biuret reaction." If albumen is precipitated with alcohol and washed with ether, it gives a deep violet color when heated with hydrochloric acid. This is "Liebermann's reaction."

III. Products of Decomposition and Digestive Action on Proteids.

1. Action of Heat alone.—When submitted to dry distillation the proteids yield the product known as Dippel's oil (see p. 796), which contains ammonium salts of the fatty acids, like butyric, valeric, and caproic, amines of the radicals of the paraffin series like methylamine, etc., aromatic compounds like aniline and phenol, and, lastly, the pyridine and quinoline bases.

2. Action of Oxidizing Agents.—Manganese dioxide and sulphuric acid or potassium bichromate and sulphuric acid acting upon the proteids produce cyanides, aldehydes, and acids of both the aromatic and the fatty groups. Nitric acid, as before stated, produces at first xanthoproteic acid, and by continued action oxybenzoic and paraoxybenzoic acids. Chlorine acting upon proteids produces, among other products, fumaric and oxalic acids. Bromine and water, when heated with proteids under pressure, cause the formation of carbon dioxide, aspartic, oxalic, and bromacetic acids, leucine, bromoform, bromanil, and other products.

3. Action of Strong Acids and Caustic Alkalies.—Prolonged boiling with sulphuric and hydrochloric acid, and fusion with caustic alkalies, give rise to practically the same products, among which are ammonia, acetic and valeric acids, amido-acids like leucine (see p. 657) and tyrosine, and indol and skatol (see p. 786).

4. Action of Dilute Mineral Acids.—Under the influence of dilute sulphuric acid (or hydrochloric acid in the presence of stannous chloride) hydrolysis ensues and a variety of products are obtained. Among these we have belonging to the class of methane derivatives leucine, aspartic acid, glutamic acid, and furfurol, and to the class of benzene derivatives tyrosine (see p. 777) and phenyl-amido-propionic acid.

5. Decomposition under the Influence of Putrefactive Ferments.—Reference was made to the decomposition of albuminoid matter under the influence of bacteria (see p. 707). The first effect on the albuminoids is a peptonization and then a

formation of products such as have been just mentioned under the two preceding cases of decomposition. In this case ammonia and hydrogen sulphide are also among the products of decomposition. In the putrefaction of gelatin or glue, instead of tyrosine, we have glycocoll as the product. Under certain pathological conditions this putrefactive change of albuminoids may take place in the intestines.

6. **Digestive Action on Proteids.**—In general, the effect of digestive action is to change proteids under the influence of enzymes into albumoses and peptones. In the digestive action of the stomach little true peptone is formed, but much albumose, while in the action of the pancreas the opposite result takes place. Very energetic action of the pancreatic ferment (see p. 704) changes the hemipeptones still further into amido-acids like tyrosine and leucine.

CLASSIFICATION OF PROTEID COMPOUNDS.

As the constitution of these compounds is still so entirely obscure, it is not possible to establish more than a provisional grouping of them. The scheme generally accepted by the best authorities is as follows :

I. **True Albuminoids,** including : 1, *Albumens ;* 2, *Globulins ;* 3, *Alkali-albuminates and Acid-albuminates ;* 4, *Coagulated Albuminoids ;* 5, *Albumoses and Peptones.*

II. **Nucleo-albumens.**

III. **Proteids,** including : 1, *Glucoproteids* (*α*, *Mucins ond Mucoids*, and *β*, *Hyalogens*) ; 2, *Chromoproteids* (*Hæmoglobins*).

IV. **Gelatinoids,** including : 1, *Keratins ;* 2, *Collagen and Glue ;* 3, *Elastin ;* and 4, *Amyloid* (*Lardacein*).

I. True Albuminoids.

These are free from phosphorus or contain it as calcium phosphate only ; are readily peptonized (with the exception of the peptones, of course) ; yield, when decomposed by acids or allowed to putrify, amido-acids ; soluble in dilute alkalies and acids (with the exception of the coagulated albuminoids). They occur in animal and vegetable tissues and liquid secretions.

1 **Albumens.**—These are soluble in water, dilute acids, and alkalies. The aqueous solution coagulates on heating in case neutral salts like sodium chloride or magnesium sulphate are present. If freed from salts (by precipitation of the insoluble

copper compound and treatment of this with strong potassium hydrate) they do not coagulate on boiling. The solution may be completely precipitated by saturating it with ammonium sulphate or with sodium chloride followed by acetic acid. As varieties of this class we may mention :

Serum Albumen occurring in the blood, chyle, and lymph. Its solutions show a specific rotatory power of —56°, and are coagulable at temperatures of from 50° to 90°, according to the solvent.

Egg Albumen is found in the white of egg. Its specific rotatory power is —35.5°, and its temperature of coagulation about 56°. White of egg contains about 12 per cent. of albumen, and may be evaporated in thin films at ordinary temperatures without losing its transparency or solubility in water.

Muscle Albumen exists in several varieties, coagulating at about 47°.

Milk Albumen (lactalbumen) is found in the milk of various animals in amount from 0.5 to 1 per cent., and remains in the whey after the coagulation of the casein by rennet. Its point of coagulation ranges from 72° to 84°.

2. **Globulins.**—These are insoluble in water, but soluble in dilute solutions of salts like sodium chloride, ammonium chloride, and sodium sulphate. The solutions coagulate on boiling, and are completely precipitated by saturation with ammonium sulphate. With the exception of vitellin, they are precipitated by saturating the solution with common salt. As varieties we have :

Vitellin.—Obtained from the yolk of egg (**Vitellus**, U. S. P.) by extracting the fats and cholesterin with ether, dissolving the white residue in common salt solution, and, after filtration, precipitating by the addition of water. It is difficult to free it from the lecithine which accompanies it in the egg yolk. It coagulates at about 75° and is lævo-rotatory.

Plant vitellins are also obtained from beans, peas, almonds, white mustard, and corn. The aleurone grains, obtained from Brazil-nuts and other sources, seem to represent a crystalline albuminoid or a compound of an albuminoid with magnesia.

Crystallin, from the crystalline lens of the eye, is probably identical with vitellin.

Myosin is the product of the clotting of muscle plasma. It coagulates in 10 per cent. sodium chloride solution at 55°–56°. The substance in the plasma generating the myosin is called *myosinogen*.

Plant myosins are also found in vegetable protoplasm.

Fibrinogen is found in blood plasma, in chyle, lymph, and serous fluids, and at times in transudations. In the clotting of blood it is converted into *fibrin*. This change takes place under the influence of a soluble fibrin ferment acting in the presence of neutral salts. It coagulates in 10 per cent. salt solution at 55°.

Serum Globulin (Paraglobulin or Fibrino-plastin) is found in blood plasma and blood serum, as well as in chyle, lymph, and serous fluids. It is incompletely precipitated by saturating the fluid with common salt. Its temperature of coagulation when in 10 per cent. sodium chloride solution is 75°.

3. Alkali-albuminates and Acid-albuminates.—Albuminoids are converted more or less rapidly by the action of alkalies and acids into the two classes above named.

The acid albuminates form jelly-like masses which, while not readily soluble in pure water, dissolve easily in acidified water. These acid solutions do not coagulate on boiling, but are precipitated by neutralization or adding neutral salts to the solution.

Syntonin is an acid albuminate prepared by the action of 0.1 per cent. hydrochloric acid upon muscle globulin. Frequently the whole class of acid albuminates are termed "syntonins."

The alkali-albuminates are not mere solutions of the albuminoids in alkali, but show a difference in percentage composition from the albuminoids from which they have been formed. This is because the alkali acts upon the albuminoid sufficiently to cause a splitting off of the nitrogen as ammonia and a loss of sulphur due to the formation of alkali sulphide.

Lieberkühn's Alkali-albuminate is a gelatinous mass insoluble in pure water, but soluble in dilute alkalies, which is obtained by the action of strong potassium hydrate solution upon egg albumen.

4. Coagulated Albuminoids.—These are formed by heating the neutral or slightly acid solutions of albumens and globulins. Prolonged action of strong alcohol also causes coagulation of proteids. The coagulated albuminoids are insoluble in water, dilute acids, and alkalies. By the action of the gastric or the pancreatic juice they are converted into peptones at the temperature of the body, and then go into solution. The coagulation of albuminoids must be distinguished from precipitation by neutralization or the addition of salts. In the latter case the precipitate still retains the properties possessed by the body when in solution; in the case of coagulation it is no longer capable of being changed back into the original proteid material.

Fibrin is formed by the action of the fibrin ferment upon fibrinogen (see p. 856). It is a white, elastic solid made up of fibre bundles.

Gluten results probably by the action of an enzyme (the gluten ferment) upon the globulin material of the flour. Gluten is, however, believed to be a mixture of *gluten-fibrin*, *gliadin* (vegetable glue), and *mucedin*.

5. Albumoses and Peptones.—Pepsin (see p. 704), in dilute hydrochloric acid solution and trypsin (see p. 703) in alkaline solution both have the power of "peptonizing" proteids. If the peptone solution so obtained be freed from unchanged albumen by coagulation and neutralization, we can in the filtrate precipitate the albumoses by saturating with ammonium sulphate, while the peptones will remain in solution. The albumoses are probably the first products of the action of enzymes upon proteids, and the continuance of the action changes them into peptones. Besides the difference in solubility in ammonium sulphate just stated, we may distinguish between the two classes also by the addition of potassium ferrocyanide to the acetic acid solution, albumoses being precipitated and peptones not, or the addition of common salt to saturation of the acetic acid solution, when albumoses are precipitated while peptones are not. At least two kinds of albumoses are to be distinguished: *anti-albumose* and *hemi-albumose*, to each of which corresponds a peptone, named therefore *anti-peptone* and *hemi-peptone* respectively. The first of these peptones cannot be further changed, while the latter (hemi-peptone) is changed by trypsin into leucine and tyrosine.

As already stated (see p. 851), the peptones, after absorption into the blood, are capable of reconversion into proteids or tissue-forming material.

The formation of poisonous albumoses, or "toxalbumens," as a product of decomposition of proteid matter in the body has already been referred to (see p. 823).

II. Nucleo-albumens.

These contain phosphorus, and, at times, also iron. They are decomposed by artificial digestion with pepsin into peptones and *nucleïns*.

1. **Vitellin**, previously described under the globulins, may belong here, as by the pepsin digestion a nucleïn is separated from it.

2. **Casein** is found only in the milk of mammalia. It is insoluble in water, soluble in dilute alkali and in an excess of

hydrochloric or sulphuric acid. The caseins of cow's milk and human milk show, however, slight differences of solubility, as well as in the appearance of the precipitate obtained by the addition of dilute acids.

Casein is not coagulated by heat alone, a film forming in this case. The ferment rennin (see p. 704), however, readily coagulates it in the presence of the accompanying calcium phosphate, as do gastric and pancreatic juice; but in milk freed from the salts normally present, rennin will not cause the formation of a curd.

The artificial digestive action of pepsin and hydrochloric acid decomposes casein at the temperature of the blood into peptone and nucleïn.

Other nucleo-albumens are found in the synovial fluid, in the kidneys, and in urine.

Nucleïns.—These are bodies containing phosphorus which are closely related to the albuminoids, and are either found in animal and vegetable cells, or are formed by the decomposition of nucleo-albumens under the influence of pepsin and hydrochloric acid. They are insoluble in alcohol and ether, scarcely soluble in water, but easily soluble in dilute alkalies. By boiling with alkalies they lose their phosphorus, which splits off as alkali phosphate. Dilute mineral acids split off at ordinary temperatures metaphosphoric acid from certain nucleïns, as in the yolk of egg and yeast. By boiling the nucleïn of yeast with dilute acids xanthine, hypoxanthine, and adenin (see p. 719) are formed.

III. Proteids.

The proteids are broken up by appropriate reagents into the two classes albuminoid and non-albuminoid compounds (carbohydrates or coloring matters). According to the character of these latter products, they may therefore be divided into two groups, *Glucoproteids* and *Chromoproteids.*

1. Glucoproteids.—These yield on decomposition with dilute acids, along with albuminoids, reducing compounds of the class of carbohydrates, or substances easily convertible into reducing carbohydrates.

a. **Mucins and Mucoids.**—The mucins are precipitated from their solutions by acetic acid, and the precipitates so obtained are not soluble in excess of the precipitant. When boiled with dilute mineral acids they yield reducing substances. The solutions of the true mucins are ropy in character. Those glucoproteids which form ropy solutions but are not

precipitated by acetic acid have been named mucoids. Mucins and mucoids are found in the submaxillary gland and the submaxillary saliva, in the mucous glands of the air-passages and of the intestines, in the umbilical cord, and in the sinews and tendons.

β. **Hyalogens.**—These are little-investigated substances which are found in the skeletons of lower forms of animal life. By the action of alkalies they are changed into *hyalines*, from which, by more complete decomposition, reducing compounds (possibly carbohydrates) are obtained.

2. Chromoproteids.—These compounds break up into albumen and coloring matter. The most important representatives of this class are the *Hæmoglobins*, or coloring matters of the blood. The parent substance of these compounds is *Oxyhæmoglobin*, as the compound of hæmoglobin with oxygen which occurs in arterial blood is called. To prepare it defibrinated blood is treated with ten times its volume of a salt solution (made by adding 1 volume of saturated salt solution to 10 volumes of water). The blood-corpuscles which settle out are freed from the salt solution by pouring this off; 2 volumes of water are added, and it is then shaken with an equal amount of ether. The ethereal layer is poured off and the aqueous layer filtered. The filtrate is precipitated by the addition of ¼ its volume of alcohol, and allowed to stand at a temperature of —5°. The composition of the oxyhæmoglobin crystals from the blood of different animals varies slightly, but the average composition is expressed by the formula $C_{600}H_{960}N_{154}FeS_3O_{179}$. Oxyhæmoglobin obtained from the blood of man and the majority of the lower animals crystallizes in prisms or rhombic plates of a beautiful blood-red color. The crystals are soluble in water, and the solution, if not too concentrated, shows two absorption bands between the lines D and E of the spectrum, which are visible with a dilution of even $\frac{1}{10000}$. At a temperature of from 60° to 70° oxyhæmoglobin splits up into albumen and hæmatin. One molecule of oxygen is held loosely combined in oxyhæmoglobin, and is given off in a vacuum or may be displaced by inert gases like nitrogen. The resulting compound is *reduced hæmoglobin*, which is present in venous blood, and results also from the putrefactive decomposition of oxyhæmoglobin. Its aqueous solution shows a broad absorption band between D and E. Hæmoglobin, by absorption of oxygen in the lungs, is changed into oxyhæmoglobin. It also combines even more readily with certain other gases, such as carbon monoxide, nitrogen dioxide, and hydrogen cyanide. *Carbon-monoxide-hæmoglobin* is a compound of 1 molecule of CO and 1 molecule of

hæmoglobin. Its aqueous solution also shows absorption bands in the spectroscope which differ in position from those of oxyhæmoglobin, being nearer the violet end of the spectrum. It may also be distinguished from oxyhæmoglobin, according to Hoppe-Seyler's test, by adding an equal volume of sodium hydrate solution of 1.3 sp. gr. The carbon monoxide compound is changed hereby to a clear red color, while ordinary blood is changed to a brownish mass.

Hæmatin, $C_{34}H_{35}N_4FeO_5$, is the colored decomposition product of the hæmoglobin. It is formed by the action of acids upon the blood, and by the decomposition of hæmin by an alkali hydrate. It is an amorphous, brownish-black powder, insoluble in water, alcohol, and ether, easily soluble in alkalies. Its alkaline solution shows a single broad absorption band extending from between C and D to near E of the spectrum. The acid solution shows several narrow bands, instead of the broad band just mentioned. Hæmatin forms a crystalline hydrochlorate, $C_{34}H_{35}N_4FeO_5.HCl$, known as *Hæmin*. These crystals are often obtained in examining dried blood-spots. The dried matter supposed to be blood is warmed in a watch-crystal with common salt and glacial acetic acid. On evaporating the solution on a water-bath characteristic crystals of hæmin are obtained. Hæmin forms a crystalline powder of silky lustre and bluish-black color, which is insoluble in water, alcohol, and ether, but soluble in dilute alkali, acidified alcohol, and hot glacial acetic acid.

By the action of concentrated sulphuric acid upon hæmatin in the presence of oxygen is formed *hæmoporphyrin*, and, by the action of the same acid upon hæmatin in the absence of oxygen, *hæmatolin*, both of which substances are free from iron.

IV. Gelatinoids.

We include here several groups of insoluble substances, which are attacked with difficulty by digestive ferments, and differ, therefore, from the other tissue-forming materials.

1. **Keratins** (or horny substances).—These compounds are found in the epithelial tissues, nails, hair, horns, and hoofs, and in feathers. They contain carbon, hydrogen, oxygen, nitrogen, and sulphur, the percentage of the last-named element varying considerably and being very loosely combined. These keratins are insoluble in water, alcohol, ether, dilute acids, and alkalies. They are hardly attacked by digestive ferments, but are decomposed by boiling with water under pressure, hydrogen sulphide

being evolved. When boiled with strong acids, leucine, tyrosine, and aspartic acid are formed.

Keratin, when prepared from feathers, forms a brownish-yellow powder, soluble in concentrated acetic acid, alkalies, and ammonia, which has been recommended for coating pills, so as to enable them to withstand the digestive liquids of the stomach, and to act only when in the intestines.

Neurokeratin is a variety which has been isolated from the nerves and brain-tissue.

Spongin is the substance of the common bath-sponge. When decomposed by acids it yields tyrosine, leucine, and glycocoll.

Silk consists of *fibroïn*, $C_{15}H_{23}N_5O_6$, which is covered with an alteration product known as *sericin* (or silk-glue), $C_{15}H_{25}N_5O_8$. The latter is easily removed by warm soap-water, and its solution so obtained constitutes the "boiled-off" liquor of the silk-dyer. Fibroïn is decomposed by acids, yielding glycocoll, alanine, leucine, and tyrosine.

Cerebrin and *Chitin*, which may be included here, have already been described (see p. 846).

2. Collagen.—The white fibres of connective tissues (sinews and tendons) are mainly composed of a substance now generally termed collagen. Its most important reaction is the change into *gelatin* when boiled with water. Bones also contain a substance, *osseïn*, which undergoes a similar change. The solutions obtained in these cases "gelatinize" or set to a jelly-like mass on cooling, and this, if carefully dried, forms the commercial gelatin, or *glue*. Solutions of gelatin are precipitated by a number of the alkaloidal reagents (see p. 804). Pepsin or trypsin converts gelatin into gelatine-peptones, and certain micro-organisms have also the power of liquefying and decomposing it. When decomposed by acids gelatin yields ammonia, glycocoll, leucine, and glutamic acid, but not tyrosine or iodol.

Hoffmeister has found that by heating gelatin for some time to 130° it loses about 0.755 per cent. of water, and becomes converted into a body in all respects identical with collagen. He therefore considers that collagen is simply the anhydride of gelatin, and ascribes to them the formulas $C_{102}H_{151}N_{31}O_{39}$ for gelatin, and $C_{102}H_{149}N_{31}O_{38}$ for collagen.

Chondrin, formerly considered to be the gelatigenous material of tissues, is now considered to be a mixture of gelatin with chondromucoid and chondroitic acid.

3. Elastin.—When connective tissue is treated with acetic acid the white fibres swell up and become transparent, whilst the elastic fibres remain unaltered, and can be seen very distinctly. Prolonged boiling with water also decomposes the collagen of the white fibres and leaves the elastin. So far as is known elastin is not soluble in any liquid which does not decompose it. It is soluble in boiling potassium hydrate, in cold concentrated sulphuric acid, and in concentrated nitric acid. It is also gradually dissolved when digested with pepsin and trypsin. With sulphuric acid it yields leucine, but no tyrosine.

4. Amyloid (Lardaceïn) is a proteid substance found under pathological conditions in the liver, spleen, kidneys, and intestines. It forms small grains somewhat resembling starch granules, whence the name. It is acted upon by pepsin and hydrochloric acid with great difficulty. When dissolved in alkalies it yields an alkali-albuminate, and with concentrated hydrochloric acid yields an acid-albuminate. It is colored reddish-brown with iodine, and violet with iodine and sulphuric acid.

CHAPTER XII.

ELECTROLYSIS AND ITS APPLICATIONS.

As regards their deportment to the electric current, fluids may be divided into three classes: (1) *those which conduct without decomposition*, as, for example, mercury and all metals in the molten state; (2) *those in which there is no transference of electrification whatever*, as in the case of many organic fluids like petroleum, turpentine, and the oils; (3) *those which undergo decomposition while conducting the current*, as diluted acids, solutions of salts of the metals, and some fused inorganic solids.

This process of decomposition or analysis by the electric current is called *electrolysis*. Those substances capable of such a decomposition are known as *electrolytes*. The conductors by which the current enters into and passes out of the solution are the *electrodes*, the former being the positive electrode, or *anode*, while the latter is the negative electrode, or *cathode*. The products of electrolytic decompositions, known as *ions*, appear only at the electrodes, and those attracted to the anode are called the *anions*, while those appearing at the cathode are the *cations*.

Modern theory assumes that the dissolved electrolyte is to a greater extent in a state of dissociation, and that the molecules are constantly gliding about, as well as their constituent atoms, which are continually separating and recombining. Under the influence of the current, these movements are controlled as to their direction, so that when an atom disengages itself from a group it is attracted towards either the anode or the cathode, where they accumulate.

Conditions of Electrolysis.—The substance to be electrolyzed must be in a liquid condition, obtained either by solution or by liquefaction. It must be a conductor, and a compound one of whose constituents is a metal. Increase of temperature increases electric conductivity and electrolytic action in fluids, while with metals the reverse is the case. When electrolysis is employed for the deposition of metals, as in electroplating, the rapidity of action greatly influences the structure of the de-

posited metal. The metallic elements separate at the cathode, hence are electro-positive, while the non-metals collect at the anode, and are therefore electro-negative. When pure, water resists the electrolytic action of the strongest currents; however, when slightly acidulated with sulphuric or hydrochloric acid, resistance is reduced and decomposition takes place readily. Since water is employed as the solvent in solutions of chemicals, their electrolysis involves the simultaneous decomposition of the water. This important factor must not be overlooked.

Secondary Reactions.—In the electrolysis of chemicals, when in solution, reactions generally occur, in which the liberated ions react with one another, with the electrolyte, or with the electrodes themselves.

Electrolysis in which the liberated ions react with the electrolyte. *Examples:*

I. $K_2SO_4 = SO_4$ (anode) $+ K_2$ (cathode).
a. $K_2 + 2H_2O = 2KOH + H_2$ (cathode).

II. $8HNO_3 = 8NO_2 + 4O_2$ (anode) $+ 4H_2$ (cathode).
a. $4H_2 + HNO_3 = NH_3 + 3H_2O$. If other acids be present, salts of ammonia result.

III. $2NH_4Cl = Cl_2$ (anode) $+ N_2 + 4H_2$ (cathode).
a. $NH_4Cl + 2Cl_2 = NCl_3 + 2H_2$.
Nitrogen Chloride.

Electrolysis in which the liberated ions react with one another:

I. $Pb(NO_3)_2 = Pb$ (cathode) $+ 2NO_2 + O_2$ (anode).
a. $Pb + O_2 = PbO_2$ (anode).
Lead Peroxide.

II. $2CuCl_2 = Cu_2$ (cathode) $+ 2Cl_2$ (anode).
a. $Cu_2 + Cl_2 = Cu_2Cl_2$.
Cuprous Chloride.

Action of Electrolytes on the Electrode.—The material of which the electrodes are composed depends largely upon the nature of the work to be performed. Such metals as copper, mercury, gold, silver, nickel, and iron are employed in special cases, while carbon (retort carbon), where applicable, is more generally used because of its cheapness and comparative resistance to the destructive action of certain gases evolved and the compounds formed. Platinum, while it resists to the greatest extent the corrosive action of acids, gases, and alkalies, is

too expensive for commercial use. We find carbon employed in the electrolytic preparation of caustic alkalies, metallic sodium, chlorinated soda, potassium chlorate, etc., while examples of the former class may be cited in the following: in the electric refining of copper, the impure metal forms the anode, while a thin strip of pure metal serves as the cathode, upon which the metal is deposited; in electroplating with such metals as gold, silver, and nickel, the anode is of the same material as we wish to deposit on the base metal which is attached to the cathode; by employing mercury as the cathode, amalgams with such metals as barium, cæsium, lithium, etc., may be obtained; metallic calcium, barium, strontium, etc., may be obtained by placing saturated solutions of their salts in a porous earthenware cup in which a strip of amalgamated platinum is suspended as the negative pole, while this is set into a graphite crucible containing hydrochloric acid, which serves as the positive electrode. Further instances will be found under the various applications of the current.

Electro-Chemical Analysis.—Metals may be deposited quantitatively from their solutions by means of electrolysis, and, when carried out under proper precautions, this method may be extended to the quantitative separation of different metals, based on their comparative electro-positive affinities. The solution containing the metal or metals is placed in a beaker and connected with the anode of a battery, which consists of a platinum spiral dipping into the fluid; suspended over this is a cone-shaped platinum cathode, upon which the metal is deposited. In other instances a platinum dish containing the solution sets on a ring of copper, which forms the cathode, while a platinum spiral suspended in the solution serves as the anode; the metal is deposited on the sides of the platinum dish, which, after washing and drying, is weighed. The least electro-positive metal is deposited first because of its proportionate weakest chemical affinity; the stronger ones follow on increasing the strength of the current. The dilution of the solution, the relative time of electrolytic action, and the strength of the current are all important factors in the successive separation of different metals from mixtures of metallic salts. The student is referred to special works on this subject.

Electrotyping.—This consists in depositing by electrolysis a layer of copper over moulds, for the purpose of reproducing engraved surfaces, also of type. In the printing of books, periodi-

cals, maps, illustrations, etc., electrotypes are made from the pages or forms after they have been set up by the printer; these reproductions are then employed for printing, and may be preserved for subsequent use. They are made by taking impressions of the type or wood-cuts by means of a press on plates composed of a mixture of beeswax and graphite, and, after trimming, the surface is brushed over with finely powdered graphite, which affords the conducting surface. These impressions are hung from copper hooks, which form the cathode, in a vat containing a strong solution of copper sulphate acidulated with sulphuric acid, and a plate of copper forms the anode. Usually two hours' immersion, using a dynamo current, is sufficient to give a coating of the desired thickness. The copper coating is then removed from the moulds, and the reverse surface filled with solder, so as to give it the necessary rigidity, after which the plates are mounted on wooden blocks.

Electroplating is the electrolytic deposition of one metal upon another. The chief metals employed for this purpose are gold, silver, nickel, copper, platinum, and such alloys as brass and German silver. For plating purposes a vat of enamelled cast iron or stoneware is used, and as anode one or more plates of the same metal which is to be deposited. These plates may be suspended from hooks of the same material. However, copper is usually employed. The articles to be plated, after scouring and washing to remove all greasy matter, are immersed in an acid bath, to rid the surface of all traces of oxide; then they are suspended in the plating solution from copper rods, which serve as the cathode. The current employed is furnished by either a dynamo or a battery, and varies in voltage according to the metal deposited. For example, in nickel-plating we begin with 5 volts, gradually decreasing the current to 1 volt; for silver-plating 3 volts are employed, with a strength of 50 ampères per square meter of cathodic surface; in gold-plating the E.M.F. should not exceed 1 volt and the current strength 10 ampères per square meter of cathodic surface. The time of immersion varies according to the metal to be plated, the metal deposited, and the thickness of the desired deposit. For nickel-plating with a battery current the time is from two to six hours, for silver from eight to twelve hours, while gold requires but a few minutes' immersion.

Heavy platings should be avoided because of their tendency to peel. The metals to be deposited in electroplating are

usually employed as double cyanides with sodium or potassium, which may be made by adding to a diluted solution of the metallic salt a solution of potassium cyanide until the precipitated metallic cyanide redissolves. Before such base metals as zinc, pewter, etc., can be plated with nickel or silver they are given a light coating of copper, in order to secure adhesion of the plating metal. In silver-plating the metal is first amalgamated by immersing in a bath of mercuric oxide and water acidulated with sulphuric acid.

Electric Refining of Metals.—This process of electrolytic refining of crude smelted metals, although of wide application, has as yet been chiefly restricted to the refinement of copper. In a vat containing a solution of copper sulphate are suspended anodes which consist of thick plates of the crude copper, while the cathodes are very thin plates of the pure metal. By means of a dynamo current thick layers of the pure metal are deposited from the solution on the cathode, while the liberated acid unites with the crude copper of the anode and keeps up the supply of sulphate as long as any metal remains. The foreign impurities with metals are deposited in the bottom of the vat.

Processes involving Electrolysis.

Electrolysis of the Alkali Chlorides.—In the electrolysis of the alkali chlorides a number of primary and secondary reactions take place, which introduce difficulties to be considered when the isolation of but one product is desired. The possible reactions are as follows :

1. Electrolysis of alkali chlorides, with formation of caustic alkalies, chlorine, and hydrogen.

a. $2NaCl = Na_2 + Cl_2$.
b. $Na_2 + 2H_2O = 2NaOH + H_2$.

2. Electrolysis of the caustic alkali formed, with liberation of hydrogen and oxygen.

a. $2NaOH = Na_2 + O_2 + H_2$.
b. $Na_2 + 2H_2O = 2NaOH + H_2$.

3. Formation of alkali hypochlorites through the action of chlorine on caustic alkalies (generated in Reaction 1).

$$2Cl + 2NaOH = NaClO + NaCl + H_2O.$$

4. Formation of chlorates through decomposition of hypochlorites.

$$3NaClO = NaClO_3 + 2NaCl.$$

5. Electrolysis of hypochlorites, with formation of caustic alkali, hydrogen, hypochlorous acid, and oxygen.

$$a.\ 2NaClO = Na_2 + Cl_2 + O_2.$$
$$b.\ 2Na + 2H_2O = 2NaOH + H_2.$$
$$c.\ H_2O + Cl + O = HClO_2.$$

6. Electrolysis of chlorates, with formation of caustic alkali, hydrogen, chloric acid, and oxygen.

$$a.\ 2KClO_3 = K_2 + Cl_2 + 3O_2.$$
$$b.\ K_2 + 2H_2O = 2KOH + H_2.$$
$$c.\ H_2O + Cl + O_2 = HClO_3.$$

7. Reduction of hypochlorites, which diffuse to the cathode, to chlorides.

$$NaClO + H_2 = H_2O + NaCl.$$

8. Reduction of chlorates, which diffuse to the cathode, to chlorides.

$$KClO_3 + 3H_2 \quad KCl + 3H_2O.$$

According to the construction of the various forms of apparatus for the electrolysis of alkali chlorides, we have two classes: the one arranges for the separation of the products of the anode and cathode by means of a diaphragm, while the second utilizes mercury as a cathode without the intervention of a diaphragm. Examples of the first class will be found in the electrolytic manufacture of arsenic, antimony, potassium chlorate, and all the various organic syntheses, while the manufacture of the caustic alkalies is a notable example of the application of the second class.

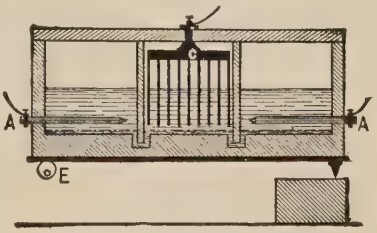
Electrolytic Preparation of Hypochlorites (Bleaching Liquid).—If a solution of an alkali chloride—for example, sodium chloride—be electrolyzed, chlorine will be liberated at the anode and sodium at the cathode. This latter reacts immediately with the water present, forming sodium hydrate, and liberates hydrogen (Reaction 1). The chlorine now reacts on the sodium hydrate, with the production of sodium hypochlorite (Reaction 3). A 10 per cent. solution of sodium chloride, after electrolytic treatment, will contain somewhat over 2 per cent. of hypochlorite and about 0.6 per cent. of chlorate, while the rest consists of unchanged chloride. This fluid is preferable for

bleaching because it is far less destructive than calcium hypochlorite and more readily removed by washing.

Electrolytic Preparation of Chlorates.—A moderately concentrated solution of potassium or sodium chloride is employed as electrolyte, to which from 1 to 5 per cent. of sodium (or potassium) carbonate is added. In the construction of the apparatus care is taken that the hydrated alkali liberated around the cathode shall be exposed to the action of the chlorine liberated from the anode, while the temperature of the fluid is kept above 50° C., which decomposes at once all hypochlorites formed (Reaction 4). The cathodes are either of iron or nickel, while the anodes are of platinum or carbon. The formation reactions involved are 1, 3, and 4, while 4 and 8 show the losses due to regeneration of the chloride.

Electrolytic Preparation of Caustic Alkalies.—Of the several electrolytic methods proposed and in use, the most ingenious and important is that of Castner. The operation is carried on in a tank which is divided into three compartments; the outside ones contain the sodium or potassium chloride brine and the carbon anodes, A A, while the inside one contains the iron cathode, C. Through this inside compartment a continuous supply of water flows, which takes up the caustic alkali produced and is conducted off into collecting tanks. The partitions are open below, just reaching to the surface of a layer of mercury which covers the entire bottom of the tank. The alkali metal (K or Na) liberated amalgamates at once with the mercury, which, through the rocking of the tank by means of the cam, E, passes into the centre compartment, where it acts as the anode during the passage of the current to the iron cathode, C; the metallic sodium (or K) of the amalgam is thereby liberated, which, reacting with the water present, gives rise to sodium (or K) hydroxide and hydrogen gas. From the two end compartments a current of chlorine gas is evolved which may be further utilized. The lye obtained from the middle (cathode) chamber contains about 20 per cent. of caustic soda (or K), which, when evaporated, yields a product 99.5 per cent. pure.

FIG. 159.



Castner's electrolytic tank.

Electrolytic Preparation of Metallic Arsenic and Antimony.—The method of Messrs. Siemens and Halske consists in first treating the native sulphides (Sb_2S_3, As_2S_3) with sodium sulphydrate (NaHS) solution, whereby soluble double salts, as sodium sulphantimonate ($Sb_2S_3 + 3Na_2S$) and sodium sulpharsenate ($As_2S_3 + 3Na_2S$), are formed. The electrolytic vat is divided into two chambers by means of a porous diaphragm; in the cathodic apartment is the above solution, while the anodic contains a solution of common salt. Sodium separates at the cathode; this decomposes the water, with liberation of hydrogen gas, which at once reunites with the sulphur and sodium to form sodium sulphydrate, while the metallic arsenic or antimony separates at the same cathode. Chlorine is evolved at the anode; this serves to hold such foreign metals as may be present (Co, Ni, Cu, Ag, Au) in solution.

Electrolytic Extraction of Gold.—According to Siemens's process, the powdered ore or tailings are extracted with a potassium cyanide solution, which is electrolyzed. Lead plates are utilized as cathodes, while iron plates serve as anodes; the gold is deposited on the surface of the former. The iron plates are gradually dissolved by the lye, giving rise to Berlin blue, which can be converted back to cyanide.

Electrolytic Preparation of White Lead.—In a wooden vat provided with a porous diaphragm is suspended an anode of lead and a cathode of copper, while the electrolyte is a solution of sodium nitrate. Through the action of the current, nitric acid is liberated at the anode, which dissolves a corresponding amount of lead, forming a solution of lead nitrate, while at the cathode metallic sodium is liberated, which decomposes in the water to sodium hydrate. These two salts react, with the production of lead hydroxide, which is allowed to digest with a solution of sodium bicarbonate, forming neutral lead carbonate. The sodium nitrate formed as by-product again electrolyzes, as above described. The sodium hydroxide formed in the last reaction is utilized for the production of bicarbonate by passing through it a current of carbonic acid gas. The reactions are as follows:

1. $NaNO_3 + H_2O = NaOH + HNO_3$.
2. $2HNO_3 + Pb = Pb(NO_3)_2 + H_2$; or,

2a. $2NaNO_3 + 2H_2O + Pb = (2NaOH + H_2) + (PbO_2(NO_2)_2)$.

3. $Pb(NO_3) + 2NaOH = Pb(OH)_2 + 2NaNO_3$.
4. $Pb(OH)_2 + NaHCO_3 = PbCO_3 + NaOH + H_2O$.

In addition to the above, the following substances can be prepared electrolytically (however, not to any extent commercially): chromium, manganese, mercury, and hydrogen. Electricity is employed in some stages of the manufacture of chlorine, copper, nickel, oxygen, silver, bismuth, cadmium, and tin, in addition to gold, arsenic, and antimony, already cited.

Ozone.—Ozone is a well-known oxidizing and bleaching agent and has many commercial applications. Its preparation is carried out on a large scale by employing a series of ozonizing tubes. The Siemens form consists of a glass tube, covered outside with tin-foil; inside of this is a smaller tube, coated with foil on its inner side. A current of oxygen is made to pass between the two tubes. The two foil coatings are connected with the poles of an induction coil the tension of which is about 13,000 volts and the interruptions from 200 to 300 per second. As a bleaching agent, it is rapid in its action, and is not so destructive as chlorine or the hypochlorites. Ozone is used as a disinfectant; also for destroying the fusel oil and aging spirits, and for aging wood for musical instruments. The micro-organisms, ammonia, and nitrites present in contaminated water may be destroyed by this agent. Ozone is used for purifying and whitening starch and dextrin.

Prussian Blue, prepared from potassium ferrocyanide and a ferrous salt, is suspended in water containing from 1 to 20 per cent. of a mineral acid, and placed in the anode chamber of an electrolytic apparatus. Through the action of the current various shades of blue may be obtained, and by prolonging electrolytic action a dark green product results.

Processes involving the Electric Furnace.

In these processes, which involve the use of the electric furnace, the current acts at an extremely high temperature on a fused mass containing the chlorides, hydroxides, or oxides of the metal to be extracted, the arrangement of the furnace varying somewhat in each case. The metals extracted by such processes on a commercial scale are potassium, sodium, and aluminum, and compounds such as carborundum and the carbides (for descriptions of these processes, see under their respective headings in the chapter on Chemistry). The metals which can be prepared thermo-electrically are boron, chromium, cobalt, wolfram, and manganese.

Thermo-Electric Preparation of the Carbides.—Through the agency of the electric furnace most metals have been made to combine with carbon to form carbides. These compounds are of the greatest value in metallurgy, owing to the influence they exert upon the hardness, tenacity, fusibility, and malleability of metals, as illustrated in the case of iron. To chemists the carbides have opened up new fields and possibilities. They are produced by heating the metallic oxides or carbonates with coke in a furnace, which consists of two blocks of limestone or burnt lime, hollowed out in the middle and securely fitted together. The carbon electrodes which pass in at the sides carry a current of 110 volts and from 1000 to 2000 ampères. Among the more important carbides are those of silicium and calcium. The former is made by fusing together sand (SiO_2), sodium chloride, and coke, and is more commonly known as carborundum (SiC). Because of its extreme hardness carborundum is used for grinding and polishing. Calcium carbide (CaC_2) is obtained by fusing together calcium carbonate and coke, and is extensively used for preparing acetylene gas, which is used as an illuminating agent.

The carbides of Li, Na, K, Ca, Ba, and Sr are decomposed by water, yielding acetylene $\left(\begin{matrix}CH\\ \|\\ CH\end{matrix}\right)$.

Aluminum and beryllium carbides react with water, yielding methane (CH_4). Manganese carbide yields, in addition, hydrogen gas.

The carbides of lanthanum, yttrium, and thorium give, with water, a mixture of acetylene, ethylene, methane, and hydrogen.

Thermo-Electric Preparation of Phosphorus.—According to the Parker process, calcium phosphate is mixed with charcoal and sand and placed in an electric furnace, so constructed that a current of coal-gas can be passed through while being heated. It is also provided with a tubular outlet, in order that the vaporized phosphorus may be carried off and condensed. The heat is generated by an electric arc. Before turning on the current, all air is driven out of the apparatus by means of coal-gas, and while in operation this current of gas serves to force the vapors of phosphorus over into a copper vessel containing water. Another method consists in the simultaneous preparation of calcium carbide, in which tricalcic phosphate is heated

in the electric furnace, with an excess of charcoal, according to the equation :

$$Ca_3(PO_4)_2 + 14C = P_2 + 3CaC_2 + 8CO.$$

Electrolytic phosphorus is pure white and of excellent quality.

Electrolysis applied to Organic Compounds.

The application of the electric current in the decomposition and synthesis of organic compounds has as yet received but comparatively limited study, yet a number of important synthetic products can be prepared electrolytically on the industrial scale. Among the organic compounds which break up most readily are the acids, or still more so their salts. The hydrogen of the carboxyl group is liberated at the negative pole, while carbon dioxide and a hydrocarbon separate at the positive ; thus, the homologues of the acetic acid series decompose as follows :

$$2C_nH_{2n+1}COOH = 2C_nH_{2n+1}COO + H_2.$$

Secondary reactions :

$$2C_nH_{2n+1}COO + H_2O = 2C_nH_{2n+1}COOH + O.$$
$$2C_nH_{2n+1}COO = C_{2n}H_{2n+2} + 2CO_2.$$
$$2C_nH_{2n+1}COO = C_nH_{2n+1}COO.C_nH_{2n+1} + CO_2.$$
$$2C_nH_{2n+1}COO + O = 2C_nH_{2n} + H_2O + 2CO_2.$$

Succinic acid.

$$C_2H_4(COOH)_2 = (C_2H_4COO)_2 + H_2.$$

Secondary reactions :

$$C_2H_4(COO)_2 + H_2O = C_2H_4(COOH)_2 + O.$$
$$C_2H_4(COO)_2 = C_2H_4 + 2CO_2.$$

Iodoform may be prepared by the electrolytic action of the current upon a mixture of alcohol (aldehyde or acetone) and an aqueous solution of an alkali or alkali earth iodide. While the reaction is going on a constant current of carbonic acid gas is being passed through the liquid.

Chloroform and **Bromoform** may be prepared in the same manner, only replacing the iodide by a chloride or bromide. The employment of carbonic acid gas is unnecessary.

Chloral.—Aldehydes may be obtained by the electrolysis of alcohol or acids. However, from an industrial stand-point, it is cheaper to produce them indirectly, with a view to preparing chloral, by the oxidizing action of chlorine obtained from the electrolysis of chlorides. In a distilling vessel provided with a diaphragm and filled with a hot solution of potassium chloride

are placed a copper cathode and a movable carbon anode which serves as a stirrer. Alcohol is gradually added to this fluid (kept at 100° C.) while electrolysis of the chloride is going on. The liberated chlorine oxidizes the alcohol to aldehyde, after which substitution takes place and hydrochloric acid gas is liberated. This is neutralized, however, in the cathodic apartment by the potassium hydrate formed in the secondary reaction. The chloral formed is recovered by distillation. In the same manner chloral may be obtained from glucose, starch, or sugar.

Nitro-Compounds.—Owing to the great technical importance of the aromatic nitro-compounds, the application of electrolysis to the reduction of these has received an unusual amount of attention. By means of oscillating electrodes, which generate nascent hydrogen, nitrobenzene may be reduced to aniline. By varying the conditions partial reduction products have been obtained, such as azoxybenzene, azobenzene, hydrazobenzene, and benzidine.

The electrolysis of aromatic nitro-compounds dissolved in sulphuric acid yields not only amido-hydrocarbons, but at the same time the hydrogen atom, which occupies the para position (to the amido group), is replaced by a hydroxyl residue. Thus, nitro-benzene yields para-amido-phenol. The homologous nitro-compounds react in like manner. Thus,—

$$C_6H_3\begin{cases}NO_2 & (1)\\ CH_3 & (4)\\ NH_2 & (5)\end{cases} \longrightarrow C_6H_2\begin{cases}NH_2 & (1)\\ OH & (2)\\ CH_3 & (4)\\ NH_2 & (5)\end{cases}.$$

Under certain conditions oxidation of the para group may take place,—

$$C_6H_4\begin{cases}NO_2 & (1)\\ CH_3 & (4)\end{cases} \longrightarrow C_6H_4\begin{cases}NH_2 & (1)\\ CH_2OH & (4)\end{cases};$$

or the group in the para position is displaced,—

$$C_6H_4\begin{cases}NO_2 & (1)\\ COOH & (4)\end{cases} \longrightarrow C_6H_4\begin{cases}NH_2 & (1)\\ OH & (4)\end{cases};$$

likewise

$$C_6H_4\begin{cases}NO_2 & (1)\\ Cl & (4)\end{cases} \longrightarrow C_6H_4\begin{cases}NH_2 & (1)\\ OH & (4)\end{cases}.$$

Saccharine.—This important product may be made electrolytically direct from the sulphone-amides. Thus, ortho-toluene-sulphone-amide $\left(C_6H_4\begin{cases}CH_3 & (1)\\ SO_2NH_2 & (2)\end{cases}\right)$ in alkaline solution

separates at the anode as saccharine, — that is, anhydro-ortho-sulphamin-benzoic acid $\left(C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>NH\right)$. Derivatives and homologues of saccharine may be prepared in like manner.

Organic Colors. — On passing the electric current, using platinum or carbon electrodes, through an aqueous solution of an aniline salt a precipitate of aniline black $[(C_6H_5N)_x]$ is obtained; likewise, under similar conditions, solutions of toluidine, alkylaniline, diphenylamine, and para-phenylene-diamine yield red, violet, and blue colors. Substitutions may be carried out by means of the current. Thus, fuchsine can be methylated by electrolyzing its hydro-methyl-alcoholic solution in the presence of potassium iodide; likewise alizarin $\left(C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_2<\begin{matrix}OH\ (1)\\OH\ (2)\end{matrix}\right)$ and purpurin $\left(C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H\ (OH)_3\right.$ 1, 2, 4) are produced at the cathode by action of the current on a mixture of anthraquinone and fused potassium hydrate.

Various tri-phenyl-methane color derivatives may be obtained by electrolyzing, in the presence of acids, such nitro-leuco bodies of the tri-phenyl-methane series as contain a nitro-group in the para position to the methane rest.* Para-rosaniline $\left(\begin{matrix}H_2NC_6H_4\\H_2NC_6H_4\end{matrix}>C<\begin{matrix}C_6H_4NH_2\\OH\end{matrix}\right)$ may be obtained by the electrolytic reduction of *p*-nitro-di-amido-tri-phenyl-methane dissolved in concentrated sulphuric acid. Electrolytically, colors of the methylene-blue group may be obtained from *p*-amido-di-methyl-aniline and its homologues. Yellows are obtainable from the aromatic oxy-acids, as gallic acid, tannin, di-oxybenzoic, gallanilid, etc. The yellow alkaline reduction products of *p*-nitro-toluene-sulphonic acid (azoxy-azo-di-nitro-stilbene-di-sulphonic acid derivatives) yield orange colors through electrolysis.

Among the natural colors, the extraction of the glucoside hæmateïn ($C_{16}H_{12}O_6$) can be much facilitated by electrolyzing an aqueous extract of logwood for one-half hour with a current of 12 amperès and 60 volts. This product is then concentrated *in vacuo* and crystallized. Brasileïn ($C_{16}H_{12}O_5$) may be obtained from Brazil-wood in like manner. Piperidine ($C_5H_{11}N$) results from the electrolytic reduction of pyridine. By this same

* *Examples:* *p*-nitro-di-amido-tri-phenyl-methane.
p-nitro-di-amido-ortho-di-tolyl-phenyl-methane.
p-nitro-di-benzyl-di-amido-o-ditolyl-phenyl-methane, etc.

reaction quinoline bases may be converted into their hydrocarbons. Of late years the current has demonstrated its value in the ferment industry ; while it assists in the culture of some organisms, it destroys others. Thus, the yeast-cells present in a mash may be protected from degeneration, while other undesirable fermentative growths may be destroyed by a careful regulation of the current.

APPENDIX.

TABLE OF ATOMIC WEIGHTS ACCORDING TO THE U. S. PHARMACOPŒIA OF 1890, TOGETHER WITH VALENCES.

NAME.	Symbol.	Atomic Weight.	Valence.
Aluminum	Al	27.04	III or $(Al_2)^{VI}$
Antimony	Sb	119.6	III, V
Arsenic	As	74.9	III, V
Barium	Ba	136.9	II, IV
Beryllium*	Be	9.03	II
Bismuth	Bi	208.9	III, V
Boron	B	10.9	III
Bromine	Br	79.76	I, III, V, VII
Cadmium	Cd	111.5	II
Cæsium	Cs	132.7	I
Calcium	Ca	39.91	II, IV
Carbon	C	11.97	IV
Cerium	Ce	139.9	$(Ce_2)^{VI}$, IV
Chlorine	Cl	35.37	I, III, V, VII
Chromium	Cr	52.0	II, $(Cr_2)^{VI}$, VI
Cobalt	Co	58.6	II, $(Co_2)^{VI}$
Columbium†	Cb	93.7	III, V
Copper	Cu	63.18	$(Cu_2)^{II}$, II
Didymium‡	Di	142.0	III, V
Erbium	Er	166.0	III or $(Er_2)^{VI}$
Fluorine	F	19.0	I
Gallium	Ga	69.9	$(Ga_2)^{VI}$
Germanium	Ge	72.3	II, IV
Gold	Au	196.7	I, III
Hydrogen	H	1.0	I
Indium	In	113.6	III or $(In_2)^{VI}$
Iodine	I	126.53	I, III, V, VII
Iridium	Ir	192.5	II, IV
Iron	Fe	55.88	II, $(Fe_2)^{VI}$, VI
Lanthanum	La	138.2	III
Lead	Pb	206.4	II, IV
Lithium	Li	7.01	I
Magnesium	Mg	24.3	II
Manganese	Mn	54.8	II, IV, VI, VIII
Mercury	Hg	199.8	$(Hg_2)^{II}$, II
Molybdenum	Mo	95.9	II, IV, VI
Nickel	Ni	58.6	II, $(Ni_2)^{VI}$
Nitrogen	N	14.01	I, III, V
Osmium	Os	190.3	II, IV, VI, VIII

* Also called Glucinum, Gl = 9.03.

† Also called Niobium, Nb = 93.7.

‡ Composed of Neo- and Praseo-Didymium.

TABLE OF ATOMIC WEIGHTS ACCORDING TO THE U. S. PHARMACOPŒIA OF 1890, TOGETHER WITH VALENCES.—(*Continued.*)

NAME.	Symbol.	Atomic Weight.	Valence.
Oxygen	O	**15.96**	II
Palladium	Pd	**106.35**	II, IV
Phosphorus	P	**30.96**	III, V
Platinum	Pt	**194.3**	II, IV
Potassium	K	**39.03**	I
Rhodium	Rh	**102.9**	II, IV
Rubidium	Rb	**85.2**	I
Ruthenium	Ru	**101.4**	II, IV, VI, VIII
Samarium	Sm	**149.62**	III, V
Scandium	Sc	**43.97**	III or $(Sc_2)^{VI}$
Selenium	Se	**78.87**	II, IV, VI
Silicon	Si	**28.3**	IV
Silver	Ag	**107.66**	I
Sodium	Na	**23.0**	I
Strontium	Sr	**87.3**	II, IV
Sulphur	S	**31.98**	II, IV, VI
Tantalum	Ta	**182.0**	III, V
Tellurium	Te	**125.0**	II, IV, VI
Terbium	Tb	**159.1**	III
Thallium	Tl	**203.7**	I, III
Thorium	Th	**231.9**	IV
Tin	Sn	**118.8**	II, IV
Titanium	Ti	**48.0**	IV
Tungsten	W	**183.6**	II, IV, VI
Uranium	U	**238.8**	II, IV, VI
Vanadium	V	**51.1**	III, V
Ytterbium	Yb	**172.6**	III
Yttrium	Yt	**88.9**	III
Zinc	Zn	**65.1**	II
Zirconium	Zr	**90.4**	IV

Thermometric Equivalents.

(*According to the Centigrade and Fahrenheit Scales.*)

C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°
—39.4	—39	—20.5	—5	—1.1	30	18	64.4	37.2	99
—39	—38.2	—20	—4	—1	30.2	18.3	65	37.7	100
—38.8	—38	—19.4	—3	—0.5	31	18.8	66	38	100.4
—38.3	—37	—19	—2.2	0	32	19	66 2	38.3	101
—38	—36.4	—18.8	—2	0.5	33	19.4	67	38.8	102
—37.7	—36	—18.3	—1	1	33.8	20	68	39	102.2
—37.2	—35	—18	—0.4	1.1	34	20.5	69	39.4	103
—37	—34.6	—17.7	0	1.6	35	21	69.8	40	104
—36.6	—34	—17.2	1	2	35.6	21.1	70	40.5	105
—36.1	—33	—17	1.4	2.2	36	21.6	71	41	105.8
—36	—32.8	—16.6	2	2.7	37	22	71.6	41.1	106
—35 5	—32	—16.1	3	3	37.4	22.2	72	41.6	107
—35	—31	—16	3.2	3.3	38	22.7	73	42	107.6
—34.4	—30	—15.5	4	3.8	39	23	73.4	42.2	108
—34	—29.2	—15	5	4	39.2	23.3	74	42.7	109
—33.8	—29	—14.4	6	4.4	40	23.8	75	43	109.4
—33.3	—28	—14	6.8	5	41	24	75.2	43.3	110
—33	—27.4	—13.8	7	5.5	42	24.4	76	43.8	111
—32 7	—27	—13.3	8	6	42.8	25	77	44	111.2
—32.2	—26	—13	8.6	6.1	43	25.5	78	44.4	112
—32	—25 6	—12.7	9	6.6	44	26	78.8	45	113
—31.6	—25	—12.2	10	7	44.6	26 1	79	45 5	114
—31.1	—24	—12	10.4	7.2	45	26.6	80	46	114.8
—31	—23.8	—11.6	11	7.7	46	27	80.6	46.1	115
—30.5	—23	—11.1	12	8	46.4	27 2	81	46.6	116
—30	—22	—11	12.2	8.3	47	27.7	82	47	116.6
—29.4	—21	—10.5	13	8.8	48	28	82.4	47.2	117
—29	—20.2	—10	14	9	48.2	28.3	83	47.7	118
—28.8	—20	—9.4	15	9.4	49	28.8	84	48	118.4
—28.3	—19	—9	15.8	10	50	29	84.2	48.3	119
—28	—18.4	—8.8	16	10 5	51	29.4	85	48.8	120
—27.7	—18	—8.3	17	11	51.8	30	86	49	120.2
—27.2	—17	—8	17.6	11.1	52	30.5	87	49.4	121
—27	—16.6	—7 7	18	11.6	53	31	87.8	50	122
—26.6	—16	—7.2	19	12	53.6	31.1	88	50.5	123
—26.1	—15	—7	19.4	12.2	54	31.6	89	51	123.8
—26	—14.8	—6.6	20	12.7	55	32	89.6	51.1	124
—25.5	—14	—6.1	21	13	55 4	32 2	90	51.6	125
—25	—13	—6	21.2	13.3	56	32.7	91	52	125.6
—24.4	—12	—5.5	22	13.8	57	33	91.4	52.2	126
—24	—11.2	—5	23	14	57.2	33.3	92	52.7	127
—23 8	—11	—4.4	24	14.4	58	33.8	93	53	127.4
—23.3	—10	—4	24.8	15	59	34	93.2	53.3	128
—23	—9.4	—3.8	25	15.5	60	34.4	94	53.8	129
—22.7	—9	—3.3	26	16	60.8	35	95	54	129.2
—22.2	—8	—3	26.6	16.1	61	35.5	96	54.4	130
—22	—7.6	—2.7	27	16.6	62	36	96.8	55	131
—21.6	—7	—2.2	28	17	62.6	36.1	97	55.5	132
—21.1	—6	—2	28.4	17.2	63	36.6	98	56	132.8
—21	—5.8	—1 6	29	17.7	64	37	98.6	56.1	133

THERMOMETRIC EQUIVALENTS.—(*Continued.*)

C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°
56.6	134	77.2	171	98	208.4	118.8	246	139.4	283
57	134.6	77.7	172	98.3	209	119	246.2	140	284
57.2	135	78	172.4	98.8	210	119.4	247	140.5	285
57.7	136	78.3	173	99	210.2	120	248	141	285.8
58	136.4	78.8	174	99 4	211	120.5	249	141.1	286
58.3	137	79	174.2	100	212	121	249.8	141.6	287
58.8	138	79.4	175	100.5	213	121.1	250	142	287.6
59	138.2	80	176	101	213.8	121.6	251	142.2	288
59.4	139	80.5	177	101.1	214	122	251.6	142.7	289
60	140	81	177.8	101.6	215	122.2	252	143	289.4
60.5	141	81.1	178	102	215.6	122.7	253	143 3	290
61	141.8	81.6	179	102.2	216	123	253.4	143.8	291
61.1	142	82	179.6	102.7	217	123.3	254	144	291.2
61.6	143	82.2	180	103	217.4	123 8	255	144 4	292
62	143.6	82.7	181	103.3	218	124	255.2	145	293
62.2	144	83	181.4	103.8	219	124.4	256	145.5	294
62.7	145	83.3	182	104	219 2	125	257	146	294.8
63	145 4	83.8	183	104.4	220	125.5	258	146.1	295
63.3	146	84	183.2	105	221	126	258.8	146.6	296
63.8	147	84.4	184	105 5	222	126.1	259	147	296.6
64	147.2	85	185	106	222.8	126.6	260	147.2	297
64.4	148	85.5	186	106.1	223	127	260.6	147.7	298
65	149	86	186.8	106.6	224	127.2	261	148	298.4
65.5	150	86.1	187	107	224.6	127 7	262	148.3	299
66	150.8	86.6	188	107.2	225	128	262.4	148.8	300
66.1	151	87	188.6	107.7	226	128.3	263	149	300.2
66.6	152	87.2	189	108	226.4	128.8	264	149.4	301
67	152.6	87.7	190	108.3	227	129	264.2	150	302
67.2	153	88	190.4	108 8	228	129.4	265	150.5	303
67.7	154	88.3	191	109	228.2	130	266	151	303.8
68	154.4	88.8	192	109 4	229	130.5	267	151.1	304
68.3	155	89	192.2	110	230	131	267.8	151.6	305
68.8	156	89.4	193	110.5	231	131.1	268	152	305.6
69	156.2	90	194	111	231.8	131.6	269	152.2	306
69.4	157	90.5	195	111.1	232	132	269.6	152.7	307
70	158	91	195 8	111.6	233	132.2	270	153	307.4
70 5	159	91.1	196	112	233.6	132.7	271	153.3	308
71	159.8	91 6	197	112.2	234	133	271.4	153.8	309
71.1	160	92	197.6	112.7	235	133.3	272	154	309.2
71.6	161	92.2	198	113	235.4	133.8	273	154.4	310
72	161.6	92.7	199	113.3	236	134	273.2	155	311
72.2	162	93	199.4	113.8	237	134.4	274	155.5	312
72.7	163	93.3	200	114	237.2	135	275	156	312.8
73	163.4	93.8	201	114.4	238	135.5	276	156.1	313
73.3	164	94	201.2	115	239	136	276.8	156.6	314
73.8	165	94.4	202	115.5	240	136.1	277	157	314.6
74	165.2	95	203	116	240.8	136.6	278	157.2	315
74.4	166	95.5	204	116.1	241	137	278.6	157.7	316
75	167	96	204.8	116.6	242	137.2	279	158	316.4
75.5	168	96.1	205	117	242.6	137.7	280	158.3	317
76	168 8	96.6	206	117.2	243	138	280.4	158.8	318
76.1	169	97	206.6	117.7	244	138.3	281	159	318.2
76.6	170	97.2	207	118	244.4	138.8	282	159.4	319
77	170.6	97.7	208	118.3	245	139	282.2	160	320

THERMOMETRIC EQUIVALENTS.—(*Continued.*)

C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°
160.5	321	181.1	358	202	395.6	222.7	433	243 3	470
161	321.8	181.6	359	202.2	396	223	433.4	243 8	471
161.1	322	182	359.6	202.7	397	223.3	434	244	471.2
161.6	323	182.2	360	203	397.4	223.8	435	244.4	472
162	323.6	182.7	361	203.3	398	224	435.2	245	473
162.2	324	183	361.4	203 8	399	224.4	436	245.5	474
162.7	325	183.3	362	204	399.2	225	437	246	474.8
163	325.4	183.8	363	204.4	400	225 5	438	246.1	475
163.3	326	184	363.2	205	401	226	438.8	246.6	476
163.8	327	184.4	364	205.5	402	226.1	439	247	476.6
164	327.2	185	365	206	402.8	226.6	440	247.2	477
164.4	328	185.5	366	206.1	403	227	440.6	247.7	478
165	329	186	366.8	206 6	404	227.2	441	248	478.4
165.5	330	186.1	367	207	404.6	227.7	442	248 3	479
166	330.8	186.6	368	207.2	405	228	442.4	248.8	480
166.1	331	187	368.6	207.7	406	228.3	443	249	480.2
166.6	332	187.2	369	208	406.4	228.8	444	249.4	481
167	332.6	187.7	370	208.3	407	229	444.2	250	482
167.2	333	188	370.4	208.8	408	229.4	445	250.5	483
167.7	334	188 3	371	209	408.2	230	446	251	483.8
168	334.4	188.8	372	209.4	409	230.5	447	251.1	484
168.3	335	189	372.2	210	410	231	447.8	251.6	485
168.8	336	189.4	373	210.5	411	231.1	448	252	485.6
169	336.2	190	374	211	411.8	231.6	449	252.2	486
169.4	337	190.5	375	211.1	412	232	449.6	252.7	487
170	338	191	375.8	211.6	413	232.2	450	253	487.4
170.5	339	191.1	376	212	413.6	232.7	451	253.3	488
171	339.8	191.6	377	212 2	414	233	451.4	253.8	489
171.1	340	192	377.6	212.7	415	233.3	452	254	489.2
171.6	341	192.2	378	213	415.4	233.8	453	254.4	490
172	341.6	192.7	379	213.3	416	234	453 2	2:5	491
172.2	342	193	379.4	213.8	417	234.4	454	255.5	492
172.7	343	193.3	380	214	417.2	235	455	256	492.8
173	343.4	193.8	381	214.4	418	235.5	456	256.1	493
173.3	344	194	381.2	215	419	236	456.8	256.6	494
173.8	345	194.4	382	215.5	420	236.1	457	257	494.6
174	345.2	195	383	216	420.8	236.6	458	257.2	495
174.4	346	195 5	384	216.1	421	237	458.6	257.7	496
175	347	196	384.8	216.6	422	237.2	459	258	496.4
175.5	348	196.1	385	217	422.6	237.7	460	258.3	497
176	348.8	196.6	386	217.2	423	238	460.4	258.8	498
176.1	349	197	386.6	217.7	424	238.3	461	259	498.2
176.6	350	197.2	387	218	424.4	238.8	462	259.4	499
177	350.6	197.7	388	218.3	425	239	462.2	260	500
177.2	351	198	388.4	218.8	426	239.4	463	260.5	501
177.7	352	198.3	389	219	426.2	240	464	261	501.8
178	352.4	198.8	390	219.4	427	240.5	465	261.1	502
178.3	353	199	390.2	220	428	241	465.8	261.6	503
178 8	354	199.4	391	220.5	429	241.1	466	262	503.6
179	354.2	200	392	221	429.8	241.6	467	262.2	504
179.4	355	200.5	393	221 1	430	242	467.6	262.7	505
180	356	201	393.8	221.6	431	242.2	468	263	505.4
180.5	357	201.1	394	222	431.6	242.7	469	263.3	506
181	357.8	201.6	395	222.2	432	243	469.4	263.8	507

THERMOMETRIC EQUIVALENTS.—(*Continued.*)

C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°
264	507.2	271.6	521	278 8	534	286.1	547	293 3	560
264.4	508	272	521.6	279	534.2	286.6	548	293.8	561
265	509	272.2	522	279.4	535	287	548.6	294	561.2
265.5	510	272.7	523	280	536	287.2	549	294 4	562
266	510.8	273	523.4	280.5	537	287.7	550	295	563
266.1	511	273.3	524	281	537.8	288	550.4	295.5	564
266.6	512	273.8	525	281.1	538	288.3	551	296	564.8
267	512.6	274	525.2	281.6	539	288 8	552	296.1	565
267.2	513	274.4	526	282	539.6	289	552.2	296 6	566
267.7	514	275	527	282.2	540	289.4	553	297	566.6
268	514.4	275.5	528	282.7	541	290	554	297.2	567
268 3	515	276	528.8	283	541.4	290.5	555	297.7	568
268.8	516	276.1	529	283 3	542	291	555.8	298	568.4
269	516.2	276.6	530	283.8	543	291.1	556	298.3	569
269.4	517	277	530.6	284	543.2	291.6	557	298.8	570
270	518	277.2	531	284.4	544	292	557.6	299	570.2
270.5	519	277.7	532	285	545	292.2	558	299.4	571
271	519.8	278	532.4	285.5	546	292.7	559	300	572
271.1	520	278.3	533	286	546.8	293	559.4		

SPECIFIC GRAVITY TABLES.

Beaumé's Scale for Liquids Lighter than Water.

The following table is calculated for a temperature of 17.5° C. (63.5° F.), and is based on the formulas $\text{B.}° + 130 = \frac{140}{\text{specific gravity}}$ and $\frac{140}{\text{specific gravity}} - 130 = \text{B.}°$

Degree Baumé.	Specific Gravity.	Degree Baumé.	Specific Gravity.	Degree Baumé.	Specific Gravity.	Degree Baumé.	Specific Gravity.
10	1.0000	33	0.8588	56	0.7526	79	0.6698
11	0.9929	34	0.8536	57	0.7486	80	0.6666
12	0.9859	35	0.8484	58	0.7446	81	0.6635
13	0.9790	36	0.8433	59	0.7407	82	0.6604
14	0.9722	37	0.8383	60	0.7368	83	0.6573
15	0.9655	38	0.8333	61	0.7329	84	0.6542
16	0.9589	39	0.8284	62	0.7290	85	0.6511
17	0.9523	40	0.8235	63	0.7253	86	0.6482
18	0.9459	41	0.8187	64	0.7216	87	0.6452
19	0.9395	42	0.8139	65	0.7179	88	0.6422
20	0.9333	43	0.8092	66	0.7142	89	0.6393
21	0.9271	44	0.8045	67	0.7106	90	0.6363
22	0.9210	45	0.8000	68	0.7070	91	0.6335
23	0.9150	46	0.7954	69	0.7035	92	0.6306
24	0.9090	47	0.7909	70	0.7000	93	0.6278
25	0.9032	48	0.7865	71	0.6965	94	0.6250
26	0.8974	49	0.7821	72	0.6931	95	0.6222
27	0.8917	50	0.7777	73	0.6896	96	0.6195
28	0.8860	51	0.7734	74	0.6863	97	0.6167
29	0.8805	52	0.7692	75	0.6829	98	0.6140
30	0.8750	53	0.7650	76	0.6796	99	0.6113
31	0.8695	54	0.7608	77	0.6763	100	0.6087
32	0.8641	55	0.7567	78	0.6731		

Baumé's Scale for Liquids Heavier than Water.

Degrees.	Baumé, 17.5° C.	Rational Baumé Scale, 12.5° C.	Degrees.	Baume, 17.5° C.	Rational Baumé Scale, 12.5° C.
	Sp. gr.	Sp. gr.		Sp. gr.	Sp. gr.
0	1.0000	1.0000	37	1.3370	1.3447
1	1.0068	1.0069	38	1.3494	1.3574
2	1.0138	1.0140	39	1.3619	1.3703
3	1.0208	1.0212	40	1.3746	1.3834
4	1.0280	1.0285	41	1.3876	1.3968
5	1.0353	1.0358	42	1.4009	1.4105
6	1.0426	1.0434	43	1.4143	1.4244
7	1.0501	1.0509	44	1.4281	1.4386
8	1.0576	1.0587	45	1.4421	1.4531
9	1.0653	1.0665	46	1.4564	1.4678
10	1.0731	1.0745	47	1.4710	1.4828
11	1.0810	1.0825	48	1.4860	1.4984
12	1.0890	1.0907	49	1.5012	1.5141
13	1.0972	1.0990	50	1.5167	1.5301
14	1.1054	1.1074	51	1.5325	1.5466
15	1.1138	1.1160	52	1.5487	1.5633
16	1.1224	1.1247	53	1.5652	1.5804
17	1.1310	1.1335	54	1.5820	1.5978
18	1.1398	1.1425	55	1.5993	1.6158
19	1.1487	1.1516	56	1.6169	1.6342
20	1.1578	1.1608	57	1.6349	1.6529
21	1.1670	1.1702	58	1.6533	1.6720
22	1.1763	1.1798	59	1.6721	1.6916
23	1.1858	1.1896	60	1.6914	1.7116
24	1.1955	1.1994	61	1.7111	1.7322
25	1.2053	1.2095	62	1.7313	1.7532
26	1.2153	1.2198	63	1.7520	1.7748
27	1.2254	1.2301	64	1.7731	1.7960
28	1.2357	1.2407	65	1.7948	1.8195
29	1.2462	1.2515	66	1.8171	1.8428
30	1.2569	1.2624	67	1.8398	1.839
31	1.2677	1.2736	68	1.8632	1.864
32	1.2788	1.2849	69	1.8871	1.885
33	1.2901	1.2965	70	1.9117	1.909
34	1.3015	1.3082	71	1.9370	1.935
35	1.3131	1.3202	72	1.9629	1.960
36	1.3250	1.3324			

What is known as the "Rational" Baumé scale is calculated by taking water at the temperature chosen at 0° B. and sulphuric acid of 1.842 specific gravity at 66° B. and using the formula $\frac{144.3}{144.3 - n^\circ} = d.$ (See Lunge's "Sulphuric Acid and Alkali," Vol. I. p. 20.)

Comparison of the Twaddle Scale with the Rational Baumé Scale.

Twaddle.	Baumé.	Specific Gravity.	Twaddle.	Baumé.	Specific Gravity.	Twaddle.	Baumé.	Specific Gravity.	Twaddle.	Baumé.	Specific Gravity.
0	0	1.000	44	26.0	1.220	88	44.1	1.440	131	57.1	1.655
1	0.7	1.005	45	26.4	1.225	89	44.4	1.445	132	57.4	1.660
2	1.4	1.010	46	26.9	1.230	90	44.8	1.450	133	57.7	1.665
3	2.1	1.015	47	27.4	1.235	91	45.1	1.455	134	57.9	1.670
4	2.7	1.020	48	27.9	1.240	92	45.4	1.460	135	58.2	1.675
5	3.4	1.025	49	28.4	1.245	93	45.8	1.465	136	58.4	1.680
6	4.1	1.030	50	28.8	1.250	94	46.1	1.470	137	58.7	1.685
7	4.7	1.035	51	29.3	1.255	95	46.4	1.475	138	58.9	1.690
8	5.4	1.040	52	29.7	1.260	96	46.8	1.480	139	59.2	1.695
9	6.0	1.045	53	30.2	1.265	97	47.1	1.485	140	59.5	1.700
10	6.7	1.050	54	30.6	1.270	98	47.4	1.490	141	59.7	1.705
11	7.4	1.055	55	31.1	1.275	99	47.8	1.495	142	60.0	1.710
12	8.0	1.060	56	31.5	1.280	100	48.1	1.500	143	60.2	1.715
13	8.7	1.065	57	32.0	1.285	101	48.4	1.505	144	60.4	1.720
14	9.4	1.070	58	32.4	1.290	102	48.7	1.510	145	60.6	1.725
15	10.0	1.075	59	32.8	1.295	103	49.0	1.515	146	60.9	1.730
16	10.6	1.080	60	33.3	1.300	104	49.4	1.520	147	61.1	1.735
17	11.2	1.085	61	33.7	1.305	105	49.7	1.525	148	61.4	1.740
18	11.9	1.090	62	34.2	1.310	106	50.0	1.530	149	61.6	1.745
19	12.4	1.095	63	34.6	1.315	107	50.3	1.535	150	61.8	1.750
20	13.0	1.100	64	35.0	1.320	108	50.6	1.540	151	62.1	1.755
21	13.6	1.105	65	35.4	1.325	109	50.9	1.545	152	62.3	1.760
22	14.2	1.110	66	35.8	1.330	110	51.2	1.550	153	62.5	1.765
23	14.9	1.115	67	36.2	1.335	111	51.5	1.555	154	62.8	1.770
24	15.4	1.120	68	36.6	1.340	112	51.8	1.560	155	63.0	1.775
25	16.0	1.125	69	37.0	1.345	113	52.1	1.565	156	63.2	1.780
26	16.5	1.130	70	37.4	1.350	114	52.4	1.570	157	63.5	1.785
27	17.1	1.135	71	37.8	1.355	115	52.7	1.575	158	63.7	1.790
28	17.7	1.140	72	38.2	1.360	116	53.0	1.580	159	64.0	1.795
29	18.3	1.145	73	38.6	1.365	117	53.3	1.585	160	64.2	1.800
30	18.8	1.150	74	39.0	1.370	118	53.6	1.590	161	64.4	1.805
31	19.3	1.155	75	39.4	1.375	119	53.9	1.595	162	64.6	1.810
32	19.8	1.160	76	39.8	1.380	120	54.1	1.600	163	64.8	1.815
33	20.3	1.165	77	40.1	1.385	121	54.4	1.605	164	65.0	1.820
34	20.9	1.170	78	40.5	1.390	122	54.7	1.610	165	65.2	1.825
35	21.4	1.175	79	40.8	1.395	123	55.0	1.615	166	65.5	1.830
36	22.0	1.180	80	41.2	1.400	124	55.2	1.620	167	65.7	1.835
37	22.5	1.185	81	41.6	1.405	125	55.5	1.625	168	65.9	1.840
38	23.0	1.190	82	42.0	1.410	126	55.8	1.630	169	66.1	1.845
39	23.5	1.195	83	42.3	1.415	127	56.0	1.635	170	66.3	1.850
40	24.0	1.200	84	42.7	1.420	128	56.3	1.640	171	66.5	1.855
41	24.5	1.205	85	43.1	1.425	129	56.6	1.645	172	66.7	1.860
42	25.0	1.210	86	43.4	1.430	130	56.9	1.650	173	67.0	1.865
43	25.5	1.215	87	43.8	1.435						

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